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Adsorption of nitrogen compounds
on zeolites

Final Report

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MICROMEDIA

ADSORPTION OF NITROGEN COMPOUNDS

ON ZEOLITES

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LIST OF SYMBOLS

a :	sorbate activity
a_n, b_n :	Fourier coefficients as defined by equations (1.31) and (1.32)
a_n^+, b_n^+ :	coefficients as defined by equation (1.40)
a_w^I, b_w^I :	coefficients as defined by equations (1.25) and (1.26) for the input signal
a_w^{II}, b_w^{II} :	coefficients as defined by equations (1.27) and (1.28) for the response signal
C :	adsorbate concentration in equation (4.2)
C_i :	adsorbate concentration (of component i) in fluid phase
$C_{i,j}^*$:	dimensionless adsorbate concentration at the i^{th} node at j^{th} time step in the finite difference scheme
C_p :	adsorbate concentration in the intraparticle void
$(C_p)_R; C_{PR}$:	adsorbate concentration in the intraparticle void at the surface of the particle
C_z :	adsorbate concentration in fluid phase
C_{ad} :	adsorbed phase concentration
$C_{ad,max}$:	maximum adsorbed phase concentration
C_{exp}^I, C_{exp}^{II} :	experimental input and response concentrations respectively
D :	diffusivity
D_0 :	corrected diffusivity
D^* :	pre-exponential factor in $D = D^* \exp(-E/RT)$
D_{ax} :	axial dispersion coefficient

D_e :	effective intraparticle diffusivity
D_v :	molecular diffusivity
$F(i\omega)$:	transfer function Fourier transformed
$F(s)$:	transfer function
$F_{calc}(t)$:	calculated response curve
$F_{obs}(t)$:	experimentally observed response curve
$f(t)$:	impulse response to a delta input
I_n :	imaginary part of F ($i n \pi / T$)
I :	imaginary part of F ($i \omega$)
K_A :	adsorption equilibrium constant
k_a, k_d :	adsorption and desorption rate constants
K_f :	external fluid film mass transfer coefficient
L :	adsorbent bed length
MB :	number of column nodes
MP :	number of particle nodes
M_n^I, M_n^{II} :	n^{th} moments of the input and response signals
M_n^{*I}, M_n^{*II} :	n^{th} weighted moments of the input and response signals
MW_i :	molecular weight of component i
N_D :	$N_D = D_{a,1} / LV$ mass dispersion number
P_{ci} :	critical pressure of gas i
q :	average sorbate concentration
R :	adsorbent particle radius
R_n :	real part of F ($i n \pi / T$)
R_ω :	real part of F ($i \omega$)
r :	radial coordinate for the particle
S :	Laplace variable
T :	half period

T_{ci} :	critical temperature of gas i
t :	time
V :	interstitial fluid velocity
y_i :	mole fraction of component i
z :	distance measured from the column inlet

Greek letters

δ_0 :	defined by equation (4.17)
δ_1 :	defined by equation (4.19)
ϵ :	root mean square error as defined in equation (1.35)
ϵ_b :	bed void fraction
ϵ_p :	intraparticle void fraction
μ :	fluid viscosity
μ_a^I, μ_a^{II} :	n^{th} central moments for the input and response signals
μ_a^{*I}, μ_a^{*II} :	n^{th} weighted central moments for the input and response signals
ρ_f :	fluid density

Dimensionless groups

Re	$2Rv\rho_f/\mu$	Reynolds number
Sc	$\mu/\rho_f D_v$	Schmidt number
Sh	$K_f 2R/D_v$	Sherwood number

INTRODUCTION

I.1 SCOPE

The heterocyclic nitrogen compounds present in crude oil cause problems such as catalyst poisoning and formation of nitrous oxides during combustion leading to environmental problems. These compounds are usually withdrawn from a given feedstock by hydrotreatment, which is a costly operation involving an expense of hydrogen at high pressure and moderately high temperature. Selective adsorption of these compounds in a packed bed may provide simple alternative for their removal from feedstocks.

Mass transfer effects such as macro, micropore diffusion, adsorption on the pore walls of adsorbents have a major influence in the efficiency of these fixed bed adsorption techniques. It is therefore essential to establish the magnitude of these parameters by experimental means. The objective of the present work is to determine the magnitude of the parameters such as effective diffusivities and adsorption coefficients for nitrogen compounds on zeolite adsorbents, using a chromatographic pulse response technique.

I.2 CHROMATOGRAPHIC PULSE RESPONSE METHOD

Chromatographic pulse response technique is used to screen the chosen adsorbents and to extract the effective diffusivities and adsorption coefficients. With this technique a small packed column of zeolites is subjected to a perturbation in the inlet concentration of the adsorbable species and the dynamic response at the column outlet is measured. In an

ideal system with plug flow and with no resistance to mass transfer, the outlet concentration should replicate the input signal with a time delay corresponding to the hold up in the column. In a real system, however, the response signal is highly dispersed. This occurs as a result of the combined effects of axial dispersion and mass transfer resistance. In essence, the time delay of the response signal contains information concerning the adsorption equilibrium and the dispersion of the response signal contains information on the sorption kinetics and the axial dispersion. In the pulse response technique this information is extracted by matching the experimental response signal to a theoretical response curve predicted from a suitable dynamic model for the system.

In the general chromatographic technique, the input disturbance to the system can be a pulse step or a periodic function [1]. Since a pulse input is the derivative of a step input, the response for a pulse input is simply the derivative of the response for a step input. Thus very similar information may be obtained from either types of experiments, and choice between those two alternatives depends entirely on practical considerations. The response curves for step inputs are commonly referred to as breakthrough curves.

Several models of varying complexity for adsorption processes have been proposed by numerous authors and are summarized by Ruthven [1]. Depending upon the characteristics of the model, various solution techniques have been investigated. Of particular importance in all of these systems is the linearity of the partial differential equations for the system model.

1.3 ADSORBENT SELECTION

The search for a suitable adsorbent is generally a first step in the development of a purification process. Commonly, the primary selection of a suitable adsorbent is accomplished by screening a range of possible adsorbents. From practical considerations the requirement for adequate adsorptive capacity restricts the choice of adsorbents for purification processes to microporous adsorbents. Among these are the traditional silicagel, activated alumina and activated carbon as well as the more recently developed crystalline aluminosilicates or zeolites. There is however a fundamental difference between these two types of adsorbents. The micropore size of zeolites is primarily determined by the crystal structure and there is virtually no distribution of pore size. In the traditional adsorbents there is a distribution of micropore size and both the mean micropore diameter and the width of the distribution about this mean are primarily determined by the manufacturing process. It is this feature that distinguishes the zeolites from the traditional microporous adsorbents.

In zeolite frameworks each aluminium atom introduces one negative charge which must be balanced by an exchangeable cation. The exchangeable cations are located at preferred sites within the framework and play a central role in the determination of adsorptive properties of the zeolites. Changing the exchangeable cation by ion exchange provides a useful means in modifying the adsorptive properties. Thus, by an appropriate choice of the zeolite framework structure, Si/Al ratio and cationic form, adsorbents with widely different adsorptive properties may be prepared. In principle, it is therefore possible to tailor the adsorptive properties to achieve the

required selectivity needed for a particular purification process. This study proposes to exploit this versatility in adsorptive properties of zeolites for the purification of heterocyclic nitrogen compounds present in crude oil feedstocks.

The nitrogen compounds present in the crudes can be roughly divided into basic and non-basic, the simplest member of each group being pyridine and pyrrole respectively.



Pyridine



Pyrrole

Strongly basic compounds such as pyridine will be adsorbed on any acid site, whereas non-basic compounds such as pyrrole will require special sites, with for example, very high acid strength. Another type of potentially good site for the adsorption of pyrrole would be the high electrostatic field existing in the vicinity of the cations in the cation exchanged zeolites. If this is the case then partial exchange would provide zeolites with both Brönsted acid sites and cationic sites which would adsorb both types of nitrogen compounds. This possibility to tailor the adsorptive properties of zeolites for a given particular separation process is what makes zeolites more attractive than the conventional microporous adsorbents. For example, the adsorption properties of a given type of zeolite may be varied by changing the distribution of acid strength (by such treatments as dealumination and steaming and in the case of pentasil zeolites by varying the Si/Al ratio during the preparation) and by changing the nature and concentration of the exchangeable cations.

Information on the nature of potential sites in zeolites for the adsorption of heterocyclic nitrogen compounds from crude oil feedstocks may be derived from temperature programmed desorption data of adsorbed bases on zeolites. Temperature programmed desorption (TPD) of adsorbed bases such as Ammonia ($pK_b = 4.75$), pyridine ($pK_b = 8.75$) and n-butylamine ($pK_b = 3.23$) has been commonly used to measure the acid site strength on surfaces [2-5]. The TPD of adsorbed bases on zeolites are characterized by the presence of two or more desorption maxima (figures I.1, I.2). Thus as shown in figures I.1 and I.2 there are two different kinds of adsorption sites present on the surface of the zeolites. The high temperature peak has been generally identified with strong acid sites. With respect to the capacity of adsorption, the adsorption sites responsible for the low temperature peak is of significant interest for the separation of nitrogen compounds present in crude since their relative contribution to the total

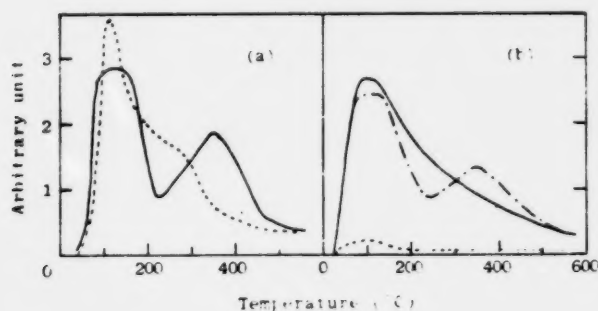


Figure I.1. Profiles of temperature programmed desorption for ammonia.

(a) --- H-ZSM5, --- HY

(b) --- Mg-ZSM5, --- H-ZSM5 steamed at 950°C. [2]

adsorption capacity is significantly higher than the adsorption capacity of the sites responsible for the higher temperature peak.

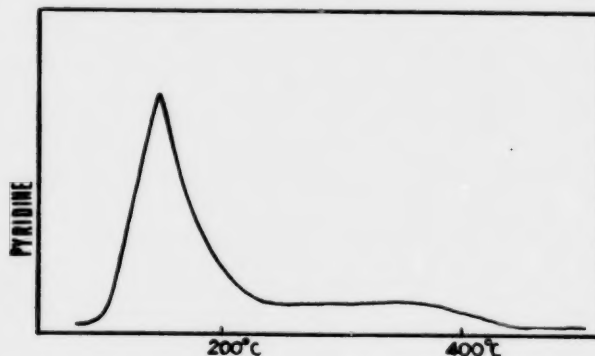


Figure I.2. TPD profile of pyridine on silica alumina.

I.4 ZEOLITES

In the present project, among the more important commercial zeolite adsorbents, zeolite X, mordenite, ZSM5 were chosen for the preliminary screening process for the purification of heterocyclic nitrogen compounds from crude oil feedstocks. The discussion below is intended to provide a brief review of the structure of these zeolites.

The building of a zeolite framework can be viewed in different ways. A convenient way is to regard the structures as constituted of assemblages of secondary building units, which are made up of several SiO_4 and AlO_4 tetrahedra. The secondary building units and some of the commonly occurring polyhedra are shown in figure I.3.

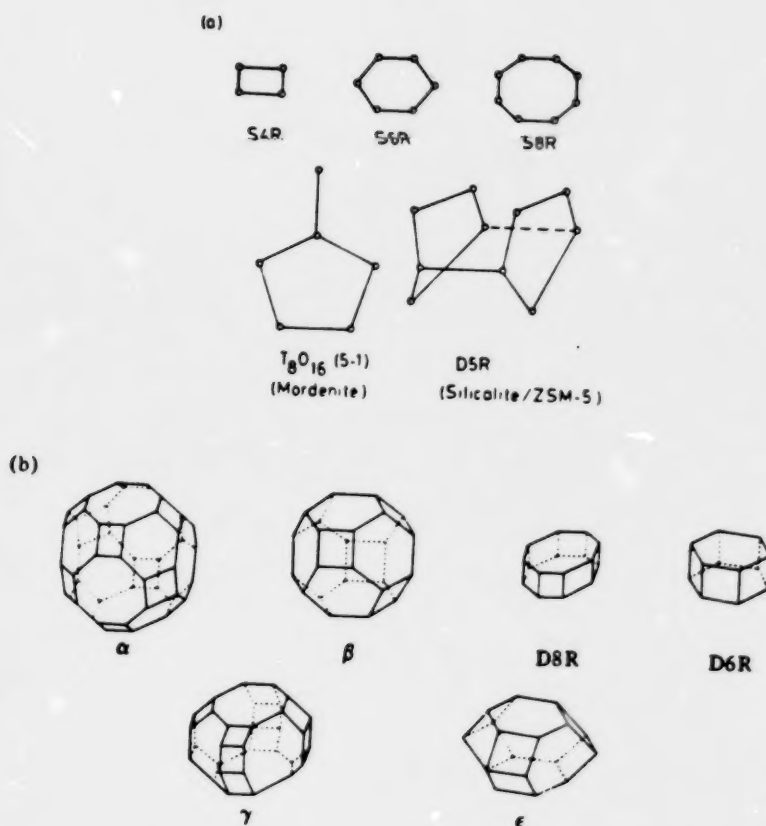


Figure I.3. (a) Secondary building units and (b) commonly occurring polyhedral units in zeolite framework structures. (Ref. [6])

1.4.1 Zeolite X (Si/Al = 1.5 - 3.0)

The framework structure of zeolite X is sketched in figure 1.4.

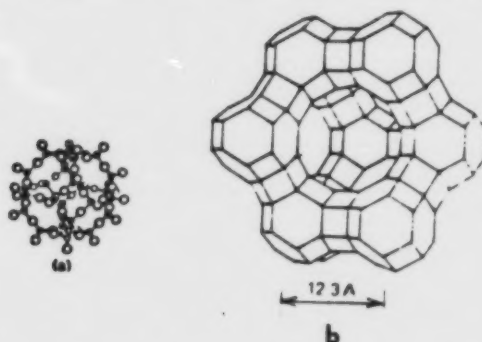


Figure I.4. Framework structure of zeolite X.

- (a) Sodalite cage structure showing individual atoms
(o - oxygen; • - aluminium or silicon)
- (b) Arrangement of sodalite units in zeolite X. (Ref. [7])

The crystallographic unit cell consists of an array of eight cages containing a total of 192 AlO_4 and SiO_4 tetrahedral units. The framework may be considered either as a tetrahedral arrangement of sodalite units connected through six membered oxygen bridges or a tetrahedral arrangement of double six ring units. As shown in figure I.4.b the stacking of sodalite cages leads to larger cavities (supercages), which contain apertures of twelve-membered rings of free diameter $\sim 7.4 \text{ \AA}$.

The various exchangeable cation positions found in zeolite X are shown in figure I.5. The S_1 site (which will offer an octahedral coordination) is located at the center of the hexagonal prisms connecting the sodalite cages. The S_1' site is located inside the sodalite cage just on the other side of the hexagonal face from the S_1 site. The S_{11} site is located in the supercage, slightly beyond the plane of the unshared hexagonal face. The S_{11}' site is its counterpart, located in the sodalite cage.

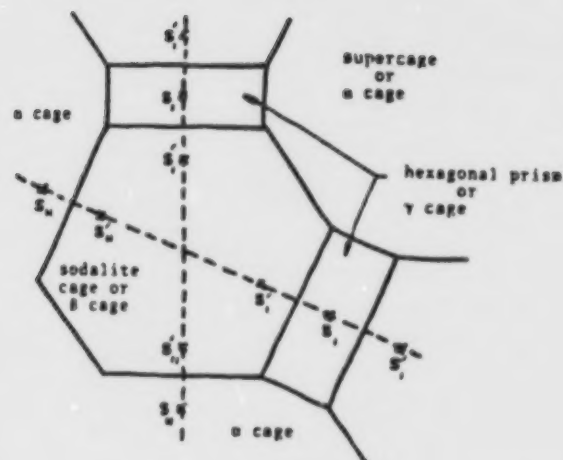


Figure 1.5. Positions of exchange sites in zeolite X. (Ref. [10])

The distribution of cations between the various sites depends both on the nature and the number of the cations and is also affected by the presence of traces of moisture.

The exchangeable cation positions have not been determined to the same extent for other zeolites as with faujasite, X, and Y.

1.4.2 Mordenite

The framework structure of mordenite can be considered as consisting of stacked T_8O_{48} units as shown in figure 1.6. The Si/Al ratio is generally close to 5.0. The aluminium content of the framework however may be decreased substantially by acid leaching without significant loss of crystallinity.

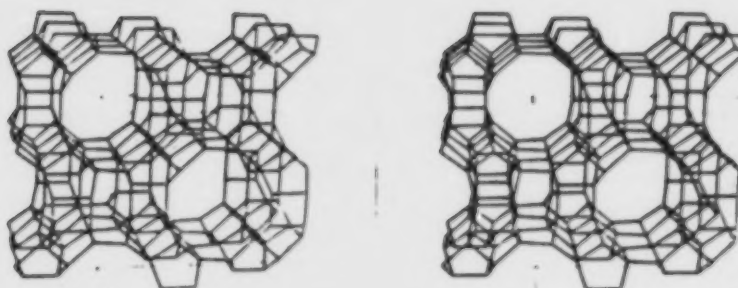


Figure 1.6. Schematic representation of the mordenite structure.
(Ref. [8])

The mordenite pore structure consists of elliptical and noninter-connected channels which are formed from twelve-membered oxygen rings having a nominal free diameter of $6.7 - 7.0 \text{ \AA}$. In the hydrogen form mordenite also offers another channel system limited by eight-membered oxygen rings with an opening of $2.9 \times 5.7 \text{ \AA}$.

The effects of pore blocking may be expected to be more serious in a one dimensional channel system as is the case with mordenite than in a three dimensional pore structure, since relatively few blocks would be sufficient to seal off the access to the interior of the crystal. Thus the presence of a small amount of extraneous material within the crystal can have a pronounced effect on the adsorptive properties of mordenite.

1.4.3 ZSM5

Pentasil zeolites in which ZSM5 is a member, represent a family of silica-rich zeolites with framework structures based on the secondary building unit D5R (Double five ring) (fig. 1.7). ZSM5 shows a unique pore structure that consists of two intersecting channel systems: one straight

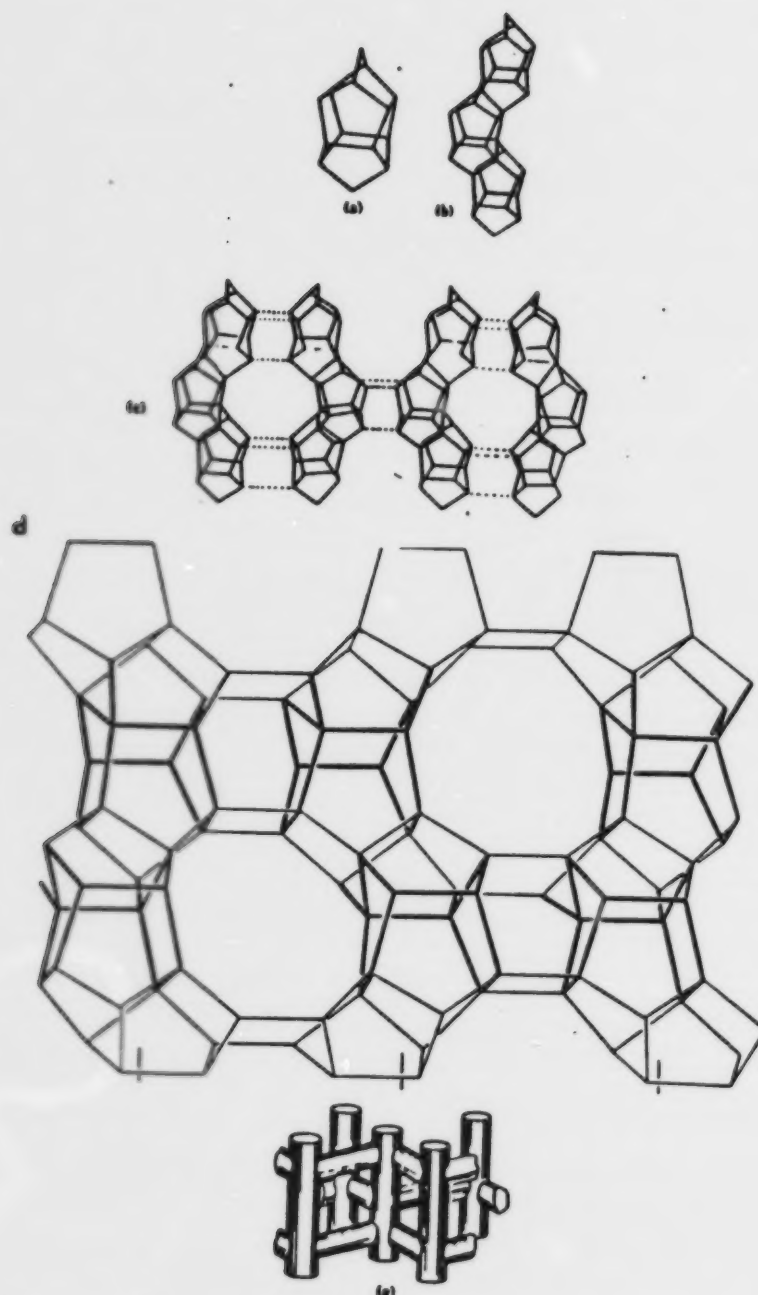


Figure 1.7. Structure of ZSM5

a) Building block; b) Linear chain obtained by the linkage of three building blocks; c) Linear-chain combination; d) A layer of Pentasil zeolite structure; e) Channel network (ref.[9]).

and the other sinusoidal and perpendicular to the former (fig. I.7). Both channel systems have ten-membered rings elliptical opening ($6 \text{ \AA}$ diameter) which is intermediate between the small pore sieves with eight-ring channels and the large pore sieves with twelve-ring channels. The Si/Al ratio of ZSM5 is typically about 30 but wide variations are possible and

this structure may be prepared also in aluminium free form ($\text{Si/Al} = \alpha$) called silicalites.

Both ZSM5 and mordenite show very high thermal, hydrothermal and acid stability. These are believed to be due to the very high Si/Al ratio and their high content of five-membered rings.

1.5 ADSORPTION IN ZEOLITES

Rates of adsorption and desorption in porous adsorbents are generally controlled by transport within the pore network rather than by the intrinsic kinetics of sorption at the surface [1,10]. According to the classical diffusion theory two regimes are defined. One is the molecular diffusion regime for which the molecular mean free path of the gaseous molecules is smaller than the pore size of the solids. When the pore size is smaller than the molecular mean free path, one is dealing with the knudsen diffusion regime and the diffusivity is inversely proportional to the pore dimension. Weisz [11] pointed out that zeolites introduces a third regime called configurational diffusion. In zeolites the transport of guest molecules is clearly effected by the close match of the size, shape and the configuration of the diffusing molecule to the corresponding parameters of the host zeolite framework. Thus in the intracrystalline pores of zeolites the diffusing molecule never escapes from the force field of the adsorbent surface and transport occurs by an activated process involving jumps between adsorption "sites". Such a process is often called "surface diffusion". However, to describe the transport of molecules in such systems a more general term "micropore" or "intracrystalline" diffusion is often used.

Accordingly, the intracrystalline diffusivity of molecules in zeolites is determined by the free diameters of the windows in the intracrystalline channel structure. In general, the zeolites may be roughly classified into small, medium and large pore zeolites. In the small pore zeolites such as zeolite A, chabazite and erionite the limiting constrictions are eight-membered oxygen rings with free diameter (4.2 Å). The medium pore zeolites (ZSM5, ZSM11, silicalite) are characterized by an intermediate channel size (5.7 Å) formed by 10 membered oxygen rings, while in large pore zeolites (X, Y, mordenite) the channel entrances are formed by twelve-membered oxygen rings, with a free diameter 7.74 Å. These window aperture values given in the literature are calculated from structural models assuming a diameter of 1.4 Å for oxygens. However, due to effects of vibrations of both the diffusing molecule and the crystal lattice the windows may be penetrated by molecules with critical kinetic diameters somewhat greater than the nominal aperture. Thus the effective diameters for unobstructed 8, 10 and 12 ring sieves may be as large as 4.5, 6.0 and 8.5 Å.

The diffusivity of molecules in zeolites can be reduced greatly by a reduction of the free diameters of the windows which can be caused by the blocking cations. The extent to which the windows are obstructed depends on the number and the nature of the cations since different cations show differing affinities for the window sites. Figure 1.8 gives a schematic representation showing the effective apertures for some cationic forms of several zeolites [6].

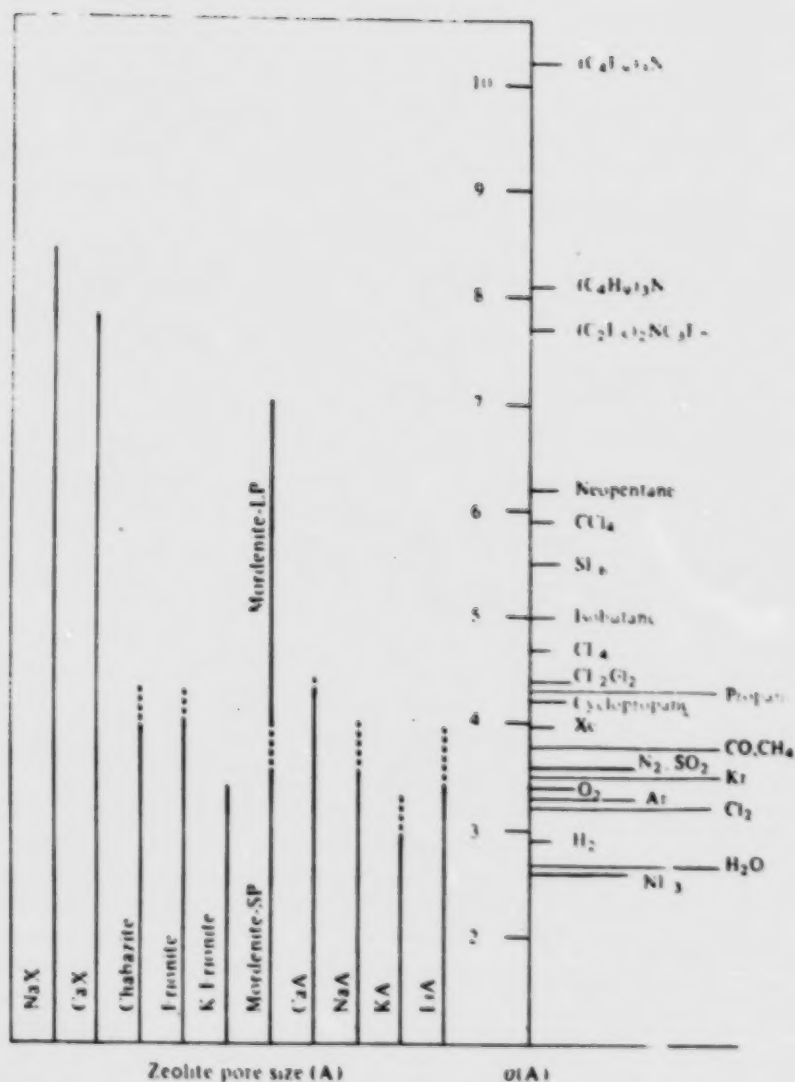


Figure 1.8. Chart showing correlation between effective pore size of various zeolites and Lennard-Jones kinetic diameter. The dotted portions indicate the range over which the cut-off occurs between low and high temperature (ref. [6]).

1.6 MATHEMATICAL MODEL FOR AN ISOTHERMAL ADSORPTION COLUMN

A mathematical solution for the response curve of an adsorption column operating isothermally and with a single-transition requires differential fluid phase and adsorbent particle mass balances. If the fluid flow is axially dispersed, its mass balance is given for a single component in an inert carrier as [1]:

$$-D_{ax} \frac{\partial^2 C_z}{\partial z^2} + \frac{\partial(vC_z)}{\partial z} + \frac{\partial C_z}{\partial t} + \left(\frac{1 - \epsilon_b}{\epsilon_b} \right) \frac{\partial \bar{q}}{\partial t} = 0 \quad (1.1)$$

where: D_{ax} is the axial dispersion coefficient

C_z is the fluid phase adsorbate concentration

Z is the axial distance from the column inlet

v is the interstitial fluid velocity

t is the time

ϵ_b is the voidage of the adsorbent bed

q is the average adsorbate concentration.

The adsorbent particle mass balance yields the adsorption rate expression:

$$\frac{\partial \bar{q}}{\partial t} = f(q, C) \quad (1.2)$$

Although represented here as one equation, the adsorption rate expression consists of one or more diffusion equations with associated boundary conditions. Depending on how the mass transfer rate is written several models with different degrees of complexity may be obtained, and the dynamic response of the column is given by the solution $C(Z,t)$, $q(Z,t)$ to equation (1.1) and (1.2) subject to the boundary conditions imposed on the column.

I.6.1 Analytical solutions

Linear systems:

For adsorption described by linear equilibrium isotherms, analytical solutions are generally available. Ruthven provides a summary of model equations and their corresponding analytical breakthrough curves for various systems (Ref. [1], Table 8.1). Ruthven notes that the analytical solutions for realistic adsorption models (2b; 3a,b; 4a,b) are too cumbersome to be of much practical use. Problems arise with the convergence of oscillating integrals which renders numerical evaluation very time consuming. However, these models do provide an insight into the adsorption system behaviour. General methods for the determination of system parameters from linear models are discussed in section I.7. These methods are generally far more efficient than the methods involving the analytical solutions to the system.

I.6.2 Nonlinear systems

For nonlinear systems analytical solutions to the breakthrough curves are not possible, however, the theoretical breakthrough curves may be calculated by numerical solution of the model equations using standard finite difference or collocation methods. Such solutions have been obtained for various cases and some of them are summarized by Ruthven (Ref. [1], Table 8.4).

I.7 GENERAL SOLUTION METHODS FOR LINEAR SYSTEMS

As previously mentioned, analytical solutions for linear, (isothermal) single-transition adsorption systems are available. Ruthven [1] notes that, although these solutions are available, most are too cumbersome to be

of much practical value. There are generally five useful techniques for the determination of response curves for linear adsorption systems. The methods include: the moment method, the weighted moment method, transfer function fitting in the Laplace domain, Fourier analysis in the frequency domain and the time domain solution method. Each of the methods has particular advantages, but the solution in the time domain has been found by many [12] to be the most accurate means for determining adsorption parameters.

The moment method was first proposed by Kubin [13] and Kucera [14] for determining adsorption parameters in packed beds using a dispersed plug flow model. For physical adsorption in packed beds, five parameters are involved: the axial fluid dispersion coefficient, the effective intraparticle diffusivity, the adsorption equilibrium constant and the adsorption rate constant. Kubin and Kucera found that all five parameters were determinable from five moments generated from a single measurement. Generating more than two moments can lead to significant errors, because of the experimental uncertainty in the frontal and tailing portions of the response curve. Thus modified methods have been proposed: the weighted moment method by Anderssen [15], transfer function fitting by Østergaard and Michelsen [16], Fourier analysis by Gangwal et al. [17] and time domain solutions by Clements [18].

1.7.1 Method of moments

For any adsorption system model, one can take the Laplace transform of the partial differential equations with corresponding boundary conditions to find the transfer function for the system. The transfer function,

$F(s)$, of the model is a function of the bed parameters and of the Laplace variable, s .

$$F(s) = f(s, \text{bed parameters})$$

The experimental transfer function may be defined as:

$$F(s) = \frac{\int_0^{\infty} C_{\text{expt}}^{\text{II}} e^{-st} dt}{\int_0^{\infty} C_{\text{expt}}^{\text{I}} e^{-st} dt} \quad (1.6)$$

where $C_{\text{expt}}^{\text{I}}$ and $C_{\text{expt}}^{\text{II}}$ are the measured input and response signals respectively.

Differentiation of equation (1.6) with respect to s gives

$$\left[\frac{dF(s)}{ds} \right]_{s=0} = M_1^{\text{I}} - M_1^{\text{II}} \quad (1.7)$$

for $s = 0$. M_1^{I} and M_1^{II} are the first moments of the input and response signals respectively. The n^{th} moment for the input and response signals are defined respectively as:

$$M_n^{\text{I}} = \frac{\int_0^{\infty} C_{\text{expt}}^{\text{I}} t^n dt}{\int_0^{\infty} C_{\text{expt}}^{\text{I}} dt} \quad (1.8)$$

$$M_n^{\text{II}} = \frac{\int_0^{\infty} C_{\text{expt}}^{\text{II}} t^n dt}{\int_0^{\infty} C_{\text{expt}}^{\text{II}} dt} \quad (1.9)$$

The second central moments or variances of the input and response signals are respectively defined as:

$$\mu_2^I = \frac{\int_0^\infty C_{\text{expt}}^I (t - M_1^I)^2 dt}{\int_0^\infty C_{\text{expt}}^I dt} \quad (1.10)$$

$$\mu_2^\Pi = \frac{\int_0^\infty C_{\text{expt}}^\Pi (t - M_1^\Pi)^2 dt}{\int_0^\infty C_{\text{expt}}^\Pi dt} \quad (1.11)$$

For a system with only two parameters to be determined, only the first and second moments of the experimental data are required to evaluate the two parameters. However, if the system model consists of more parameters, higher moments are necessary. Kubin [13] and Kucera [14] showed that, in principle, for a first order reversible system with five determinable parameters, all are determinable from a single experiment by generating five moments. Unfortunately, the moment method has the disadvantage that the weighting factor, t^2 , puts a large weight on the tailing portion of the signal. Thus with higher moments, errors are magnified manifold.

Schneider and Smith [19] proposed a method for evaluating the five parameter Kubin-Kucera adsorption model from first and second moments based upon a series of measurements with various flow rates and particle sizes.

Recently, Hyun and Danner [20] used the method of moments for the evaluation of adsorption equilibrium constants and diffusivities for ethane and ethylene in biporous zeolites. Their equilibrium data was found to be in excellent agreement with data obtained by static methods.

1.7.2 The Weighted Moment Method:

Østergaard and Michelsen [16] proposed that a weighting factor, $t^n e^{-st}$, should be used to overcome the shortcomings of the moment method. It should be noted that this factor is zero both initially and after long periods of time. Thus the weighted moment equations are defined as:

$$m_n^* = \frac{\int_0^\infty C t^n e^{-st} dt}{\int_0^\infty C dt} \quad (1.12)$$

$$\mu_n^* = \frac{\int_0^\infty C (t - m_1^*/m_0^*)^n e^{-st} dt}{\int_0^\infty C dt} \quad (1.13)$$

where m_n^* is the n^{th} weighted moment and μ_n^* is the n^{th} weighted central moment. The second central moment is then related to the first and zeroth moments by:

$$\mu_2^* = m_2^* - (m_1^*/m_0^*)^2 \quad (1.14)$$

The moments are related to the transfer function as follows:

$$\frac{m_0^{*II}}{m_0^{*I}} = F(s) \quad (1.15)$$

$$\frac{m_1^{*II}}{m_0^{*II}} - \frac{m_1^{*I}}{m_0^{*I}} = - \frac{F'(s)}{F(s)} \quad (1.16)$$

$$\frac{m_2^{*II}}{m_0^{*II}} - \frac{m_2^{*I}}{m_0^{*I}} = \frac{d}{ds} \left[\frac{F'(s)}{F(s)} \right] \quad (1.17)$$

Thus n parameters may be determined from any n weighted moment equations. The problem then arises for the choice of s . Anderssen and White [15] have suggested that the optimal value of s depends upon the order (n) of the moment

$$s = \frac{n_{\text{highest}}}{t_{\text{max,input}} + t_{\text{max,output}} - \Delta t_D} \quad (1.18)$$

where t_{max} is the time that the respective signal reaches its maximum value and t_D is the difference in time delay between the signals.

Skopp [21] reevaluated the use of the weighted moment method by determining an optimal truncation point when using the method of moments. He found that there was little advantage in using the weighted moment method.

I.7.3 Transfer Function Fitting

Østergaard and Michelsen [16] showed that for a simple system having only two determinable parameters (the mean residence time, $\bar{\tau}$; and the dispersion number, N_D) that these parameters could be determined by transfer function fitting. For their system model, the transfer function is given by:

$$F(s) = \exp \left\{ \frac{1}{2N_D} [1 - (1 + 4N_D \bar{\tau} s)^{1/2}] \right\} \quad (1.19)$$

They showed that the parameters could be determined from a plot of $-\ln(F(s))^{-1}$ versus $s[\ln(F(s))]^{-2}$ according to the equation:

$$-\ln(F(s))^{-1} = \bar{\tau} s [\ln(F(s))]^{-2} - N_D \quad (1.20)$$

or by plotting $[F'(s)/F(s)]^{-2}$ versus s according to the equation:

$$\left[\frac{F'(s)}{F(s)} \right]^{-2} = \frac{4N_D s}{\bar{\tau}} + \bar{\tau}^{-2} \quad (1.21)$$

The problem here is the choice of s . Hopkins et al. [22] recommended that fitting should be done within the range $2 \leq \bar{\tau} s \leq 5$. The method of transfer function fitting, however, has not been extended to more complex systems.

I.7.4 Fourier Analysis Method

Gangwal et al. [17] applied Fourier analysis to estimate parameters from chromatographic pulse response data using various models with different degrees of complexity.

The method of Fourier analysis assumes that the input and response signals may be represented by numerous harmonic components. Fourier analysis then evaluates the decay in amplitude and the phase shift for the harmonic components between the input and response signals.

The transfer function for a system can be Fourier transformed by substituting $s = i\omega$ into the transfer function, ω being the frequency. Thus,

$$F(i\omega) = R_{\omega} + i I_{\omega} \quad (1.22)$$

where R and I are the real and imaginary components respectively, which are functions of the system parameters. The Fourier transformed transfer function derived from the experimental input and response signals is given by:

$$F(i\omega) = \frac{\int_0^{\infty} C_{\text{expt}}^{\text{II}} e^{-i\omega t} dt}{\int_0^{\infty} C_{\text{expt}}^{\text{I}} e^{-i\omega t} dt} \quad (1.23)$$

which may be more conveniently represented by:

$$F(i\omega) = \frac{a_{\omega}^{\text{II}} - ib_{\omega}^{\text{II}}}{a_{\omega}^{\text{I}} - ib_{\omega}^{\text{I}}}$$

where:

$$a_{\omega}^{\text{I}} = \int_0^{\infty} C_{\text{expt}}^{\text{I}} \cos(\omega t) dt \quad (1.25)$$

$$b_{\omega}^{\text{I}} = \int_0^{\infty} C_{\text{expt}}^{\text{I}} \sin(\omega t) dt \quad (1.26)$$

$$a_{\omega}^{\text{II}} = \int_0^{\infty} C_{\text{expt}}^{\text{II}} \cos(\omega t) dt \quad (1.27)$$

$$b_{\omega}^{\text{II}} = \int_0^{\infty} C_{\text{expt}}^{\text{II}} \sin(\omega t) dt \quad (1.28)$$

For the simple two parameter model used by Fahim and Wakao [12], the system parameters can be determined directly by equating equations (1.22) and (1.24). The parameters involved in the real and imaginary parts of the equation (1.22) are determined in terms of the Fourier coefficients evaluated from the signals measured.

1.7.5 Time Domain Solution Methods

In the time domain solution method the model parameters are determined by minimizing the error between experimental and calculated response signals using a suitable optimization technique. In the time domain method, the following methods may be used to predict the response signal to a given input to the chromatographic column.

1.7.5.1 Prediction by a Convolution Integral

The response curve to a given input may be calculated from the input signal ($C_{exp}(t)$) and the impulse response of a delta input ($f(t)$) according to the convolution integral:

$$C_{calc}^I(t) = \int_0^t C_{exp}^I(t) \cdot f(t - \xi) d\xi \quad (1.29)$$

$f(t)$ is the Laplace inversion of the transfer function defined as

$$\int_0^\infty f(t) \exp(-st) dt = F(s) \quad (1.30)$$

For very simple cases the transfer function can be Laplace inverted easily using conventional methods. However, in many cases the transfer functions are more complicated and the Laplace inversion by conventional techniques becomes difficult. In these situations, the inversion may be performed in terms of a Fourier series.

$$f(t) = \frac{a_0}{2} + \sum_{n=1}^{\infty} a_n \cos \frac{n\pi t}{T} + b_n \sin \frac{n\pi t}{T} \quad (1.31)$$

where:

$$a_n = \frac{1}{T} \int_0^{2T} f(t) \cos \frac{n\pi t}{T} dt \quad (1.32)$$

$$b_n = \frac{1}{T} \int_0^{2T} f(t) \sin \frac{n\pi t}{T} dt \quad (1.33)$$

and $2T$ is a period of time sufficiently long for the tailing portion of the response signal to "die out".

On the other hand substitution of $s = in\pi/T$ into equation (1.30) gives:

$$\begin{aligned} F(in\pi/T) &= \int_0^{\infty} f(t) e^{-in\pi t/T} dt \\ &= \int_0^{\infty} f(t) \cos \frac{n\pi t}{T} dt - i \int_0^{\infty} f(t) \sin \frac{n\pi t}{T} dt \quad (1.34) \\ &= R_n - i I_n \end{aligned}$$

The terms on the left hand side of the equation may be integrated from 0 to $2T$ instead of 0 to ∞ and equation (1.31) may be rewritten in terms of R_n and I_n evaluated from the transfer function as:

$$f(t) = \frac{1}{2T} + \frac{1}{T} \sum_{n=1}^{\infty} R_n \cos \frac{n\pi t}{T} - I_n \sin \frac{n\pi t}{T} \quad (1.35)$$

The response curve may then be calculated from equations (1.29) and (1.34). The parameters may be regarded as correct when the calculated and experimental response curves are identical. The comparison may be made over the

entire region or any arbitrary time interval [23]. To compare the response signals, a root mean square (RMS) error between C_{expt} and C_{calc} is often employed [24].

$$\epsilon = \frac{\int_0^{2T} (C_{\text{expt}}^{\text{II}} - C_{\text{calc}}^{\text{II}})^2 dt}{\int_0^{2T} (C_{\text{expt}}^{\text{II}})^2 dt} \quad (1.36)$$

Wakao et al. [25] used this technique for an adsorbable tracer (air) signal imposed on a packed bed of porous (monodisperse) particles. There were five system parameters to be evaluated: the axial dispersion coefficient, D_{ax} ; the effective diffusivity, D_e ; the adsorption equilibrium constant, K_A ; the adsorption rate constant, k_a ; and the particle to fluid mass transfer coefficient. With a correlation for D_{ax} and assuming that k_a was infinitely large, the values for the remaining three parameters were determined by a three-dimensional search.

1.7.5.2 Prediction by a Fourier series

Alternatively, the input signal ($C_{\text{expt}}(t)$) and the response signal ($C_{\text{calc}}(t)$) may be expressed in terms of Fourier series.

$$C_{\text{expt}}^{\text{I}}(t) = \frac{a_0}{2} + \sum_{n=1}^{\infty} \left(a_n \cos \frac{n\pi t}{T} + b_n \sin \frac{n\pi t}{T} \right) \quad (1.37)$$

$$C_{\text{calc}}^{\text{I}}(t) = \frac{a_0^+}{2} + \sum_{n=1}^{\infty} \left(a_n^+ \cos \frac{n\pi t}{T} + b_n^+ \sin \frac{n\pi t}{T} \right) \quad (1.38)$$

where a_n , b_n , a_n^+ and b_n^+ are defined in the usual manner. The transfer function may be written:

$$F(s) = \frac{\int_0^{\infty} C_{\text{calc}}^{\text{II}} \exp(-st) dt}{\int_0^{\infty} C_{\text{expt}}^{\text{I}} \exp(-st) dt} \quad (1.39)$$

Substituting $s = in\pi/T$ into (I.39) with the response signal being zero for time greater than $2T$.

$$F(in\pi/T) = \frac{\int_0^{2T} C_{calc}^{\Pi} \exp(-in\pi/T) dt}{\int_0^{2T} C_{expt}^I \exp(-in\pi/T) dt} \quad (1.40)$$

From (I.39) and (I.40), it can be shown that:

$$a_n^+ - ib_n^+ = (a_n - ib_n) F(in\pi/T) \quad (1.41)$$

Thus the Fourier coefficients for (I.38) are evaluated by the experimental input curve and the transfer function. If the experimental response signal ($C_{expt}(t)$) is expressed in terms of a Fourier series, then the RMS error can be used to determine the correct parameter values.

II. EXPERIMENTAL

II.1 PREPARATION OF ZEOLITES

Mordenite and zeolite X were obtained from commercial sources.

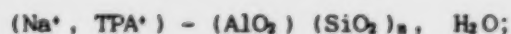
<u>Zeolite</u>	<u>Source</u>
H - Mordenite	Norton Chemicals
Na - Mordenite	Norton Chemicals
Na - X	Strem Chemicals

Ca - Mordenite, H - X and Ca - X were prepared in the laboratory by ion exchange methods. The procedure is described in section II.2. ZSM5 was synthesized at the laboratory. The description of the procedure is reproduced below from a laboratory manuel (in French).

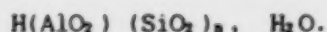
II.2 SYNTHESIS OF ZSM5

La composition des zéolites synthétisées est formulée de la façon suivante:

1) pour la forme dite précurseur:



2) pour la forme dite active ou acide:



Description de la méthode de synthèse:

La méthode de synthèse utilisée a été mise au point par Z. Gabelica et al. [26], et désignée comme la méthode B'.

Le milieu de réaction a la composition molaire typique suivante:

SiO_2	: Na_2O	: Al_2O_3	: H_2SO_4	: TPABr	: NaCl	: H_2O
96.5	28.8	x	17.3	8.9	47.1	1.888

Selon le rapport molaire Si/Al désiré pour le produit final, la quantité x d' Al_2O_3 est choisie grâce à une courbe de calibration $(\text{Si}/\text{Al})_{\text{pré}}$, en fonction de $(\text{Si}/\text{Al})_{\text{réact.}}$ établie dans notre laboratoire pour la méthode B'.

Réactifs utilisés

La source de silice (SiO_2) est constituée par du silicate de sodium, communément appelé "Waterglass" fourni par la compagnie Lawrason, de Québec, sous le nom de "silicate soda" brand Q. Sa composition pondérale déterminée par absorption atomique est de:

(28.9% SiO_2 , 7.1% Na_2O , 64% H_2O).

- la source d'aluminium est du sulfate d'aluminium $\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O}$ de la compagnie Anachemia;
- la base organique: le bromure de tetrapropylammonium (TPABr) de pureté 98% provient de la compagnie Aldrich;
- le chlorure de sodium (NaCl), réactif ACS provient de la compagnie Anachemia;
- l'acide sulfurique (H_2SO_4) de pureté 95-98%, réactif ACS est de la compagnie Fisher.

Préparation du gel alumino-silicique:

La procédure suivie comporte les étapes suivantes:

pour une base de 100 g de silicate de Na:

- 1) préparation d'une solution A (basique) de 100 g de silicate de Na dans 50 mL d'eau;
- 2) préparation d'une solution acide B en mélangeant dans l'ordre suivant, $\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O}$ (quantité variable calculable à partir des résultats du tableau II.1), 50 mL H_2O , 8.5 g de H_2SO_4 (on laisse refroidir) et 12 g de TPABr;
- 3) préparation d'une solution C de NaCl dans 50 mL H_2O ;
- 4) on verse lentement et simultanément les deux solutions A et B dans la solution C tout en agitant suffisamment pour homogénéiser et tout en maintenant le pH entre les valeurs 2 et 4.

On procède ainsi jusqu'à épuisement de la solution acide B. A ce moment, à peu près la moitié de la solution A a été utilisée;

- 5) on laisse réagir pendant environ 2 heures sous agitation;
- 6) on verse ensuite lentement le reste de la solution A, le pH s'élevant alors jusqu'à une valeur comprise entre 9 et 10;
- 7) une fois la solution A épuisée, on laisse réagir pendant 2 heures;
- 8) on verse le mélange réactionnel dans des autoclaves en acier inoxydable munies d'un revêtement interne en Teflon;
- 9) on place les autoclaves dans une étuve à 140°C;
- 10) on agite manuellement 3 fois par jour, les nuits étant exclues.

L'autoclave est maintenue à 140°C pendant 6 à 7 jours, période suffisante en général pour que la cristallisation du gel soit complète. Cel-

le-ci se manifeste notamment par le dépôt du produit cristallisé au fond de l'autoclave, laissant un liquide clair surnageant.

Lavage du précurseur:

Le lavage s'effectue par centrifugation dans une centrifugeuse à panier de marque IEC CS Compact Centrifuge, à l'aide d'eau distillée. L'intérieur du panier est tapissé d'une double couche de papier filtre Whatman 542. Le contenu des autoclaves est versé lentement dans le panier, celui-ci tournant à environ 4000 tr/min, de façon à avoir un gâteau de zéolithe uniforme. On ajuste ensuite le débit d'eau distillée de façon à maintenir une couche d'eau en permanence par-dessus le gâteau.

On laisse s'écouler l'eau jusqu'à ce que le pH de l'eau de lavage avoisine celui de l'eau distillée.

Pour 100 g de zéolithe, il faut environ 20 gallons d'eau distillée et l'opération de lavage dure de 8 à 10 heures. Une fois lavé, on met le panier à sécher à 130-140°C à l'étude, une nuit (~ 12-13 h.). Finalement, on décolle le gâteau de zéolithe séché, du papier filtre et on pulvérise celui-ci par broyage. On a alors la forme "précurseur" de la zéolithe.

Activation de la zéolithe:

Celle-ci a lieu en 3 étapes:

Calcination du précurseur. La calcination du précurseur est effectuée dans un four sous air statique à 500-530°C afin d'éliminer la base organique TPABr qui obstrue les pores de la zéolithe. De cette façon on libère les canaux et l'échange des ions Na^+ est alors possible. Notons que le précurseur est placé dans le four à température ambiante afin d'éviter tout choc thermique et une décomposition partielle du réseau cristallin. Le four est alors chauffé lentement jusqu'à 500°C (environ 6 heures) et maintenu à cette température pendant 12 à 15 heures.

La décomposition sous air de la base organique dans la zéolithe commence vers 360°C et se termine vers 425°C [26]. Une fois la calcination terminée, on arrête le chauffage et on laisse refroidir dans le four jusqu'à la température ambiante.

Echange ionique $\text{Na}^+/\text{NH}_4^+$. Il s'agit ici de substituer les contre-ions Na^+ inclus dans la zéolithe par des ions ammonium NH_4^+ . Pour cela on procède à 3 échanges successifs en contactant la zéolithe avec une solution 1 M de nitrate d'ammonium $\text{NH}_4^+ \text{NO}_3^-$ à environ 80°C. La proportion est de 50 à 100 mL de solution par g de zéolithe. Pour 180 g de zéolithe (production typique de précurseur), on utilise 10 litres de solution pour chaque échange.

L'échange avait lieu dans une cuve en Pyrex. Le chauffage était assuré par une plaque chauffante, et l'agitation par un agitateur mécanique. L'échange terminé, on laisse refroidir à une température inférieure à

40°C puis on procède à un lavage identique à celui du précurseur. Les deux premiers échanges sont suivis d'un lavage succinct avec environ 6 à 7 gallons d'eau distillée. Le dernier lavage a lieu avec 20 à 25 gallons d'eau distillée.

L'analyse des zéolithes montre que ces 3 échanges et le dernier lavage sont suffisants pour éliminer tout le sodium.

Calcination de la forme NH_4^+ . La dernière étape consiste en une calcination identique à celle de la première étape de l'activation. Ainsi les ions NH_4^+ sont convertis et remplacés par des protons H^+ selon la réaction



On a alors la forme active de la zéolithe: H-ZSM5.

II.3 X-RAY DIFFRACTION ANALYSIS

X-ray powder diffraction patterns of the zeolites were measured with a Phillips pw 1010 X-ray diffractometer equipped with a Goniometer (Phillips pw 1050). A copper source ($\lambda = 1.54050 \text{ \AA}$) was used and the X-ray tube was operated at 40 Kv and 20 mA.

II.4 POROSITY MEASUREMENTS

Macroporosity of the pelletized zeolite aggregates was measured by mercury porosimetry (Quantachrome system).

II.5 BULK DENSITY MEASUREMENTS

Bulk densities of the zeolites are required to evaluate the bed voidages. Bulk density of the zeolite aggregates was measured by mercury displacement method. The glass apparatus used is given in figure II.1.

Procedure:

- a) With the sample container lowered, enough mercury is added to the system so that the mercury level is at the reference mark on the stem of the glass reservoir and on the readable position of the measuring buret near the 2 mL level. With both stopcocks open the reading on the measuring buret is noted (V_1).
- b) The sample container is then raised and with the aid of a vacuum the mercury is transferred over to the buret and the reservoir A. The stopcock B on the sample container is then closed and the vacuum is released.
- c) Approximately 1 g of zeolite is then weighted accurately (W) and is placed in the sample container. The stopcock B is then opened slowly until the mercury is flowed back to the reference mark. The elevation of the sample container is then adjusted to the new mercury level in the buret.

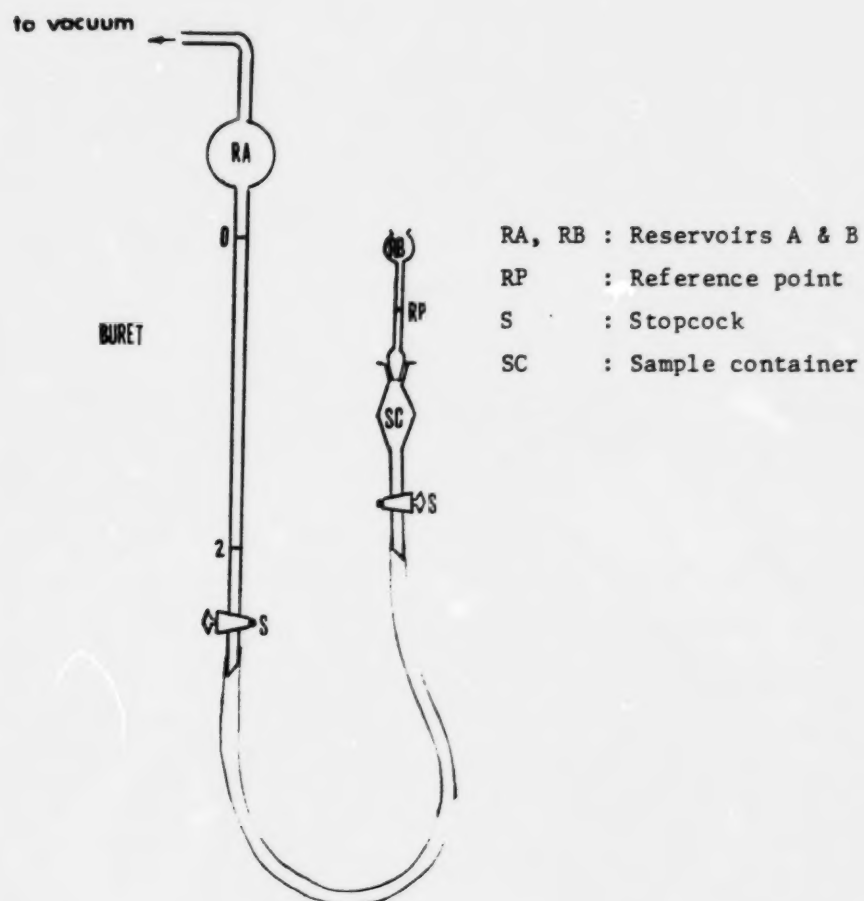


Figure II.1. Glass apparatus for bulk density measurements.

- d) The system is then vibrated using a hand held vibrator and the mercury level is adjusted to the reference level as needed. Vibration is continued until no further change is observed. With the stopcocks open and with the mercury level at the reference mark, the buret reading is noted (V_2).

Calculation:

Bulk density:

$$B = \frac{W}{V_2 - V_1} \text{ (g/cc)}$$

where: W = sample weight (g)

V_1 = initial buret reading (cc)

V_2 = final buret reading (cc).

II.6 CHROMATOGRAPHIC PULSE ANALYSIS METHOD

A chromatographic technique is used to investigate the effective diffusivities of nitrogen compounds in zeolites. In this technique a small packed column of zeolite is subjected to perturbation in the form of a pulse of the adsorbable species (Nitrogen Compounds) and the dynamic response at the column outlet is measured.

The chromatographic system used (fig. II.2) is based on a "Varian 3300" gas chromatograph equipped with a thermal conductivity detector (TCD). Helium was used as the carrier gas. The carrier gas flow rate through the adsorption column was measured with a soap bubble meter located at the outlet of the TCD detector. The carrier gas was first flowed through a heated sample injection port (the temperature of the sample in-

jection port was controlled by the varian gas chromatograph) where the nitrogen compounds could be injected to the carrier gas stream by means of an injection valve (Valco 4 port) or by a syringe. The carrier gas stream was then flowed through a preheater column maintained at the same temperature as the adsorption column, before entering the reference side of the TCD detector. The carrier gas emerging from the reference side of the detector was flowed through the adsorption column and the sample side of the TCD detector. The single carrier gas flow arrangement is expected to minimize the susceptibility of the TCD output to the carrier gas flow and pressure fluctuations, and also this particular arrangement permitted us to monitor both the input and output signal. The TCD output signal was monitored using a HP 3392 A integrator and a Linear Inst. Corp. recorder. The analog recorder output signals obtained were digitized using a HP 7475 A plotter and a IBM PC microcomputer. (A brief description of the digitizing program used and a program listing is given in appendix 1).

The adsorption column used was a 15 cm long and 4.6860 mm inside diameter, stainless steel tube. The columns were packed with zeolite particles that were sieved to 40-60 mesh in most cases.

The zeolite samples were calcined at 500°C in an oven for 8 hr prior to their packing into the chromatographic adsorption column. A weighted amount of the calcined sample was then packed into the stainless steel tube (15 cm x 0.625 cm). After installation of the adsorption column in the gas chromatographic oven, the zeolite sample was further heat

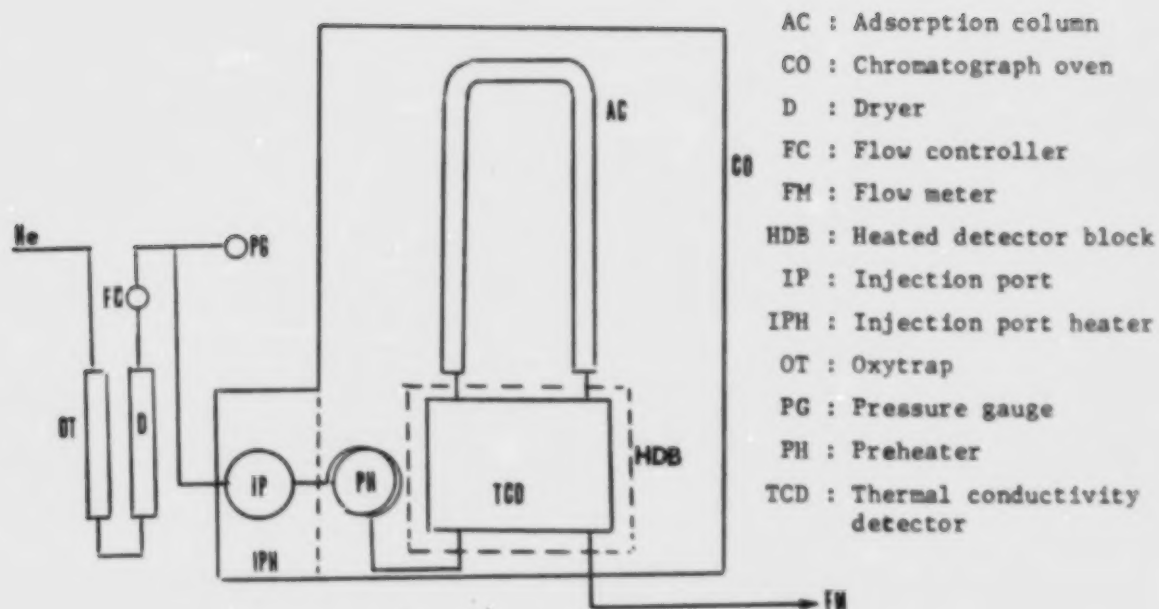


Figure II.2. Schematic diagram of the experimental set up.

treated *in situ* for an overnight period (16 hr) at 375°C (maximum permitted temperature of the chromatographic oven is 400°C) under a flow of dry helium. After this period, the oven temperature and flow rates were established at the desired values for the chromatographic pulse experiments.

III. RESULTS

III.1 X-RAY POWDER DIFFRACTION DATA

X-ray powder diffraction data of some of the zeolite adsorbents are given in the appendix II along with literature reported data. No changes in the X-ray diffraction data are occurred as a result of ion exchange processes.

III.2 PULSE RESPONSE DATA

The analysis of pulse response chromatographic data is essentially based on the matching of the experimentally obtained chromatographic response curves to the theoretical response curves predicted by an appropriate dynamic model. In the past various models have been proposed and various methods of analysis of chromatographic data based on these models are discussed in section I.7. All these methods essentially assume system linearity. This assumption is valid for most systems provided that the concentration change over which the response signal is measured is sufficiently small. Thus, prior to the use of such models a rigorous test should be done to establish the system linearity. In the linear regime the normalized response signal is independent of the magnitude of the pulse size and a variation of the pulse size provides a direct and simple means of verifying the system linearity.

III.2.1 Linearity tests with pyridine/Na-mordenite system

Preliminary tests to establish the system linearity were conducted with the pyridine/Na-mordenite system. Retention time data for pyridine are listed in table III.1. A first observation is the large irreversible uptake of pyridine by this system. Secondly, the tabulated retention time

data for pyridine (table III.1) indicate a significant influence of the inlet pulse size on the response signal. This suggests that under the operating conditions used the behaviour of the pyridine/Na-mordenite is nonlinear. For a 1 μ L pyridine pulse the retention time of pyridine is significantly lower (2-3 min) than the retention time for a pyridine pulse of 0.6 μ L (15 min). At very low pulse sizes (below 0.5 L) the response signal either does not appear at all or is broadened into the background. In general the response signals are characterized by a finite, very long tail with a very small height above the baseline. Preliminary tests also indicated that the effect of the pulse size on the response signal could not be removed by operating at very low pulse sizes. At low pulse sizes ($\approx$ 0.5 μ L) the response signal becomes broadened into the background, thus making the use of such small pulse volumes impractical.

The essential observation of this preliminary study is the nonlinear behaviour of the pyridine/Na-mordenite system under operating conditions. Also it was established that the system does not approach linearity for low injection volumes that are practical. Thus under practical operating conditions the system (pyridine/Na-mordenite) behaviour is nonlinear and linear chromatography theory could not be applied to describe the experimental data.

Extensive tests were made with several other pyridine/zeolite systems. The general behaviour of these systems parallels the behaviour of the pyridine/Na-mordenite system, described above. All systems investigated exhibit a nonlinear behaviour under practical operating conditions.

Bed parameters:

Weight of adsorbent : 1.65 g

Packed bed length : 13 cm

Particle size : 10 - 50 mesh

Table III.1 - Retention times of pyridine in Na-Mordenite.

Operational conditions: 100°C; 15 cc/min (He).

Pulse size (μ L)	Inlet pulse (min)	Retention time (min)	Area: Inlet pulse (counts)	Area: Response signal (counts)
1	0.28	2.34	3.34×10^6	1.66×10^6
1	0.28	2.74	3.35×10^6	2.66×10^6
1	0.28	2.82	3.33×10^6	2.69×10^6
1	0.28	3.05	3.52×10^6	1.57×10^6
0.8	0.28	4.24	2.63×10^7	1.19×10^7
0.8	0.28	5.53	2.67×10^6	1.22×10^6
0.6	0.28	15.5	1.99×10^6	9.20×10^5
0.6	0.29	14.4	1.71×10^6	7.64×10^5
0.2	Response pulse either does not appear completely or is broadened into the background.			

III.2.2 Pyridine/H-mordenite system

Experimental results obtained with the pyridine/H-mordenite system are summarized in tables III.2 - III.7 and in figures III.1 - III.6 for various flow rates and temperatures. As described above the pyridine/H-mordenite system also is characterized by a large irreversible uptake of pyridine (0.033 g.pyridine/g.zeolite). From preliminary tests it was established that the system is nonlinear under operating conditions. Tables III.2 - III.7 show the elution times for pyridine at peak maximum and the percentage of pyridine that could be recovered in the response signal (figures in brackets). The percentage recovery figures always remain below 100%. These lower figures partially resulted from an incomplete integration of the response signal, caused by the presence of a finite long tail in the response signal, with a very small height. However, within a given series of experiments, the recovery data could be compared, since the integration times were similar. In table III.2, the sections A, B, C, D & E represent the data obtained on different days. It can be seen immediately, that the first injection of the day to an already pyridine saturated bed which was on a He stream overnight is considerably broadened (fig. III.1 A1, B1 & C1)* than subsequent pulses. Also, the retention times are longer and the recovery figures are much smaller than for subsequent pulses. These data indicate a partial desaturation of the bed on stream. Also, it was observed that the retention time of pyridine is sensitive to whether a given pulse is injected soon after elution of the previous pulse or after a finite length of time. In other words the retention

* The pulse response data for the 1st pulse of the day are not given in sections D & E. The runs reported in these sections were done after first saturating the bed with a large volume pulse of pyridine.

time of pyridine is sensitive to the time interval between two consecutive pulses. With short time intervals the elution time for the second pulse is shorter. For this reason, to obtain reproducible chromatographic response data the interval between consecutive pulses were carefully controlled. However, even with a careful control, the chromatographic pulse response data are not exactly reproducible (see tables III.2 - III.17 and figures III.1 - III.25).

The effect of flow rate and temperature on the response signal can be seen from a comparison of figures III.1 and III.2 and figures III.3-III.6. The increase in both flow rate and temperature caused a decrease in the elution times for the peak maxima. At higher temperatures (fig. III.6) the tailing of the response signal is much less pronounced than at lower temperatures and the response signals appear to be somewhat sharper.

III.2.3 Pyridine/Na-mordenite system

Experimental results obtained with this system are given in tables III.8 - III.12 and in figures III.7 - III.11. The system is nonlinear under operating conditions. However, the behaviour of the pyridine/Na-mordenite system differs somewhat from that of the pyridine/H-mordenite system. Firstly, the reproducibility of the data were poor. This lack of reproducibility is associated with the slow desorption of pyridine from the bed. Secondly, an increase in the flow rate had no important effect on the retention of the pyridine pulse. On the other hand, the temperature of the bed had a significant effect on the response signal. An increase in the

System: Pyridine/H-mordenite (Fig. III.1)

Bed parameters:

Weight of adsorbent : 1.5 g
 Packed bed length : 12.5 cm
 Particle size : 28/32 mesh

Table III.2 - Retention times of pyridine in H-mordenite.
 (Injection volume 1 μ L)

Operational conditions: 100°C; 15 cc/min (He).

Run	Inlet pulse (min)	Retention time (min)	Area: Inlet pulse (counts)	Area: Response signal (counts)
A) 1	0.27	19.44	3.23×10^6	1.28×10^6 (40%)
2	0.26	9.70	3.16×10^6	1.84×10^6 (58%)
B) 1	0.28	19.27	3.20×10^6	5.68×10^5 (18%)
2	0.28	5.56	3.20×10^6	1.90×10^6 (27%)
3	0.28	3.92	3.20×10^6	1.90×10^6 (60%)
4	0.28	5.63	3.20×10^6	1.26×10^6 (39%)
C) 1	0.28	18.46	3.22×10^6	4.26×10^5 (13%)
2	0.28	3.40	3.21×10^6	1.23×10^5 (38%)
3	0.28	3.49	3.11×10^6	1.81×10^6 (58%)
4	0.28	3.49	3.11×10^6	1.04×10^6 (39%)
D) 1	0.28	2.80	3.16×10^6	2.28×10^6 (72%)
2	0.28	2.73	3.17×10^6	2.26×10^6 (71%)
3	0.28	2.71	3.15×10^6	2.05×10^6 (65%)
E) 1	0.27	4.05	3.23×10^6	1.13×10^6 (35%)
2	0.28	2.54	3.18×10^6	1.80×10^6 (56%)
3	0.28	2.36	3.21×10^6	1.82×10^6 (56%)
4	0.28	1.75	3.18×10^6	1.29×10^6 (40%)

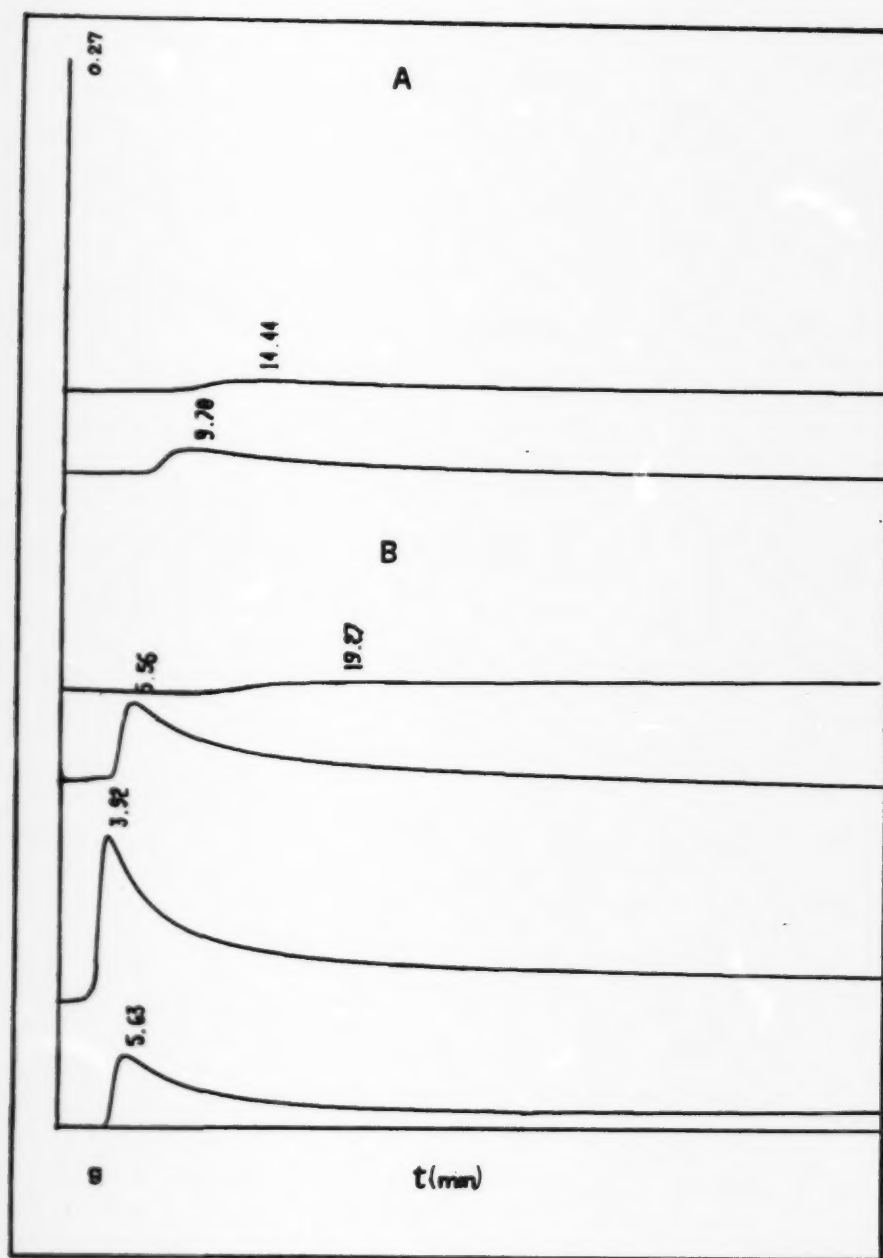


Figure III.1. Experimental chromatograms for the pyridine/H-mordenite system (15 cc/min; 100°C; 1 μ L).

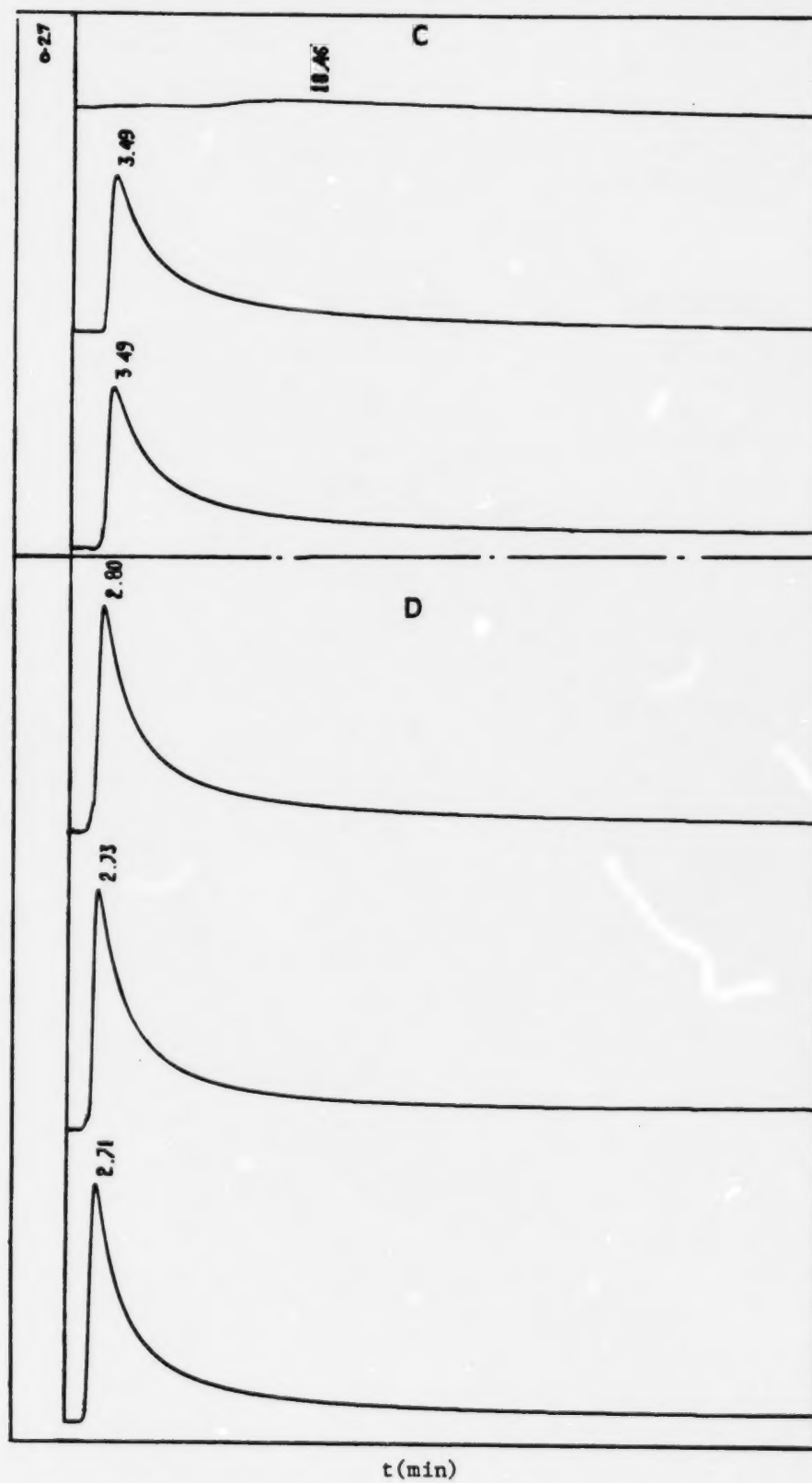


Figure III.1. (Continued)

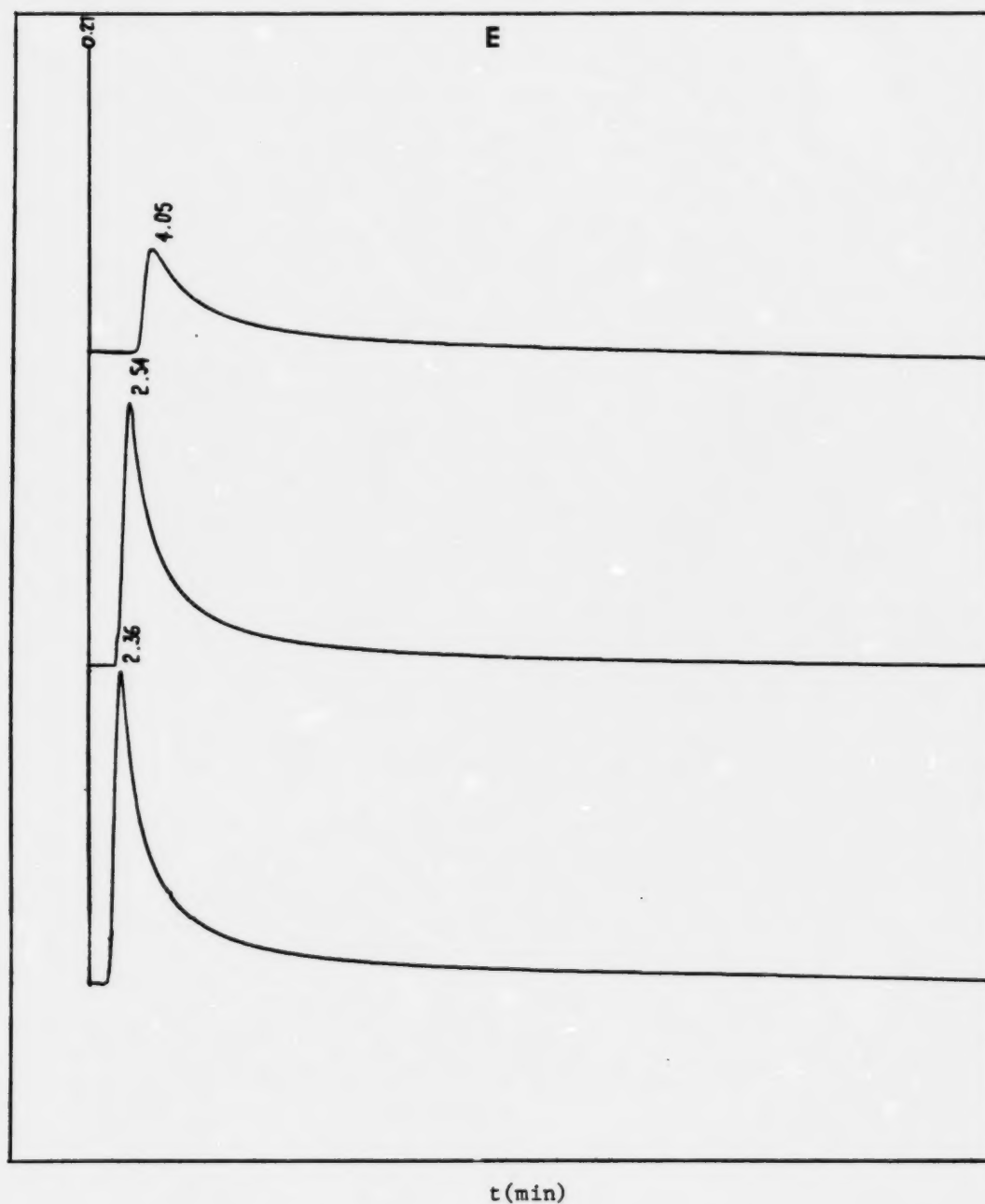


Figure III.1. (Continued)

Table III.3 - Retention times of pyridine in H-mordenite.
(Injection volume: 1 μ L)

Operational conditions: 100°C; 30 cc/min (He).

Inlet pulse (min)	Retention time (min)	Area: Inlet pulse (counts)	Area: Response signal (counts)
0.14	0.80	1.59×10^6	1.56×10^6 (98%)
0.14	0.96	1.58×10^6	1.18×10^6 (75%)
0.14	0.93	1.62×10^6	1.16×10^6 (71%)

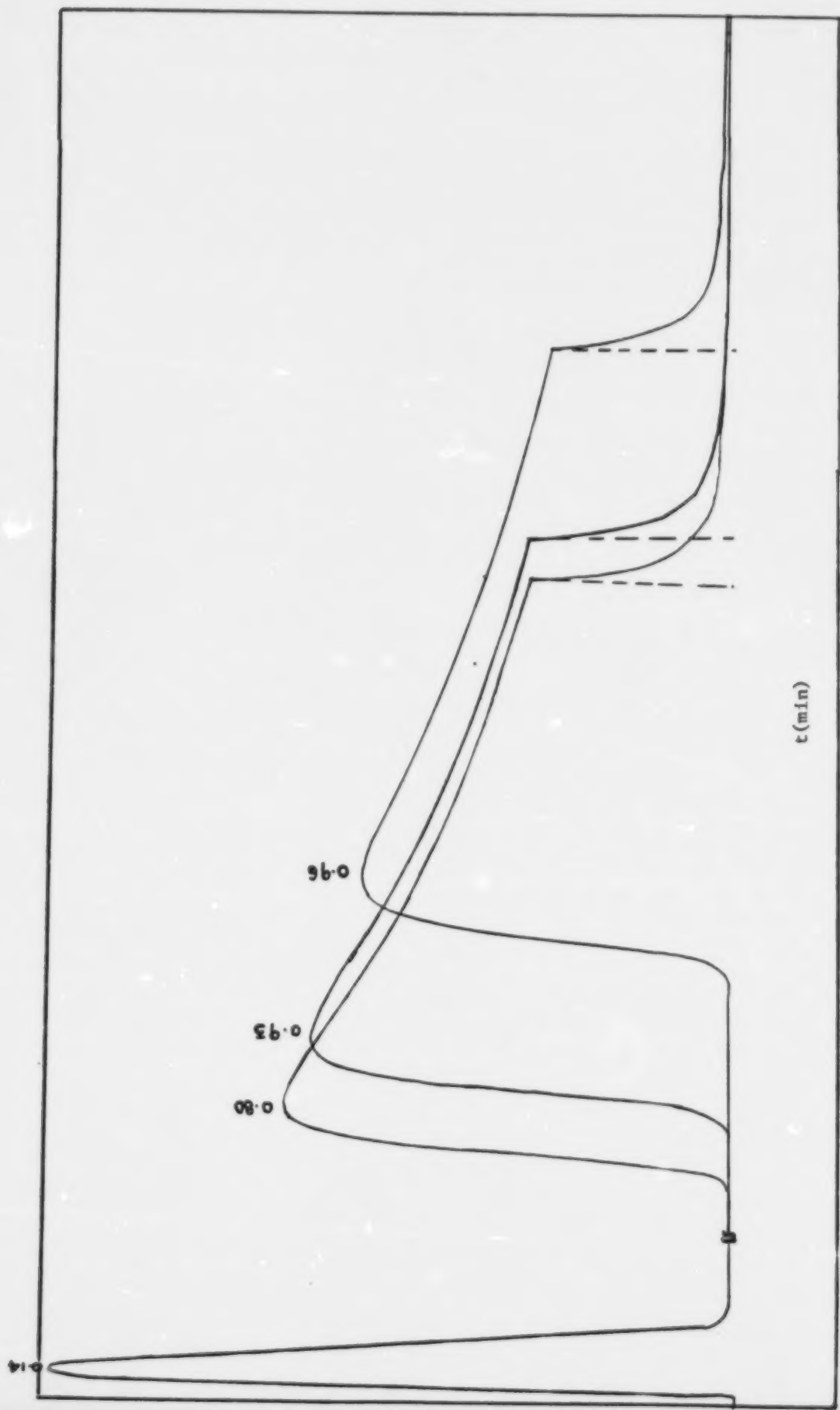


Figure III.2. Experimental chromatograms for the pyridine/II-mordenite system (30 cc/min; 100°C; 1 μ L).

System: Pyridine/H-mordenite (Fig. III.3)

Bed parameters:

Weight of adsorbent : 1.40 g

Packed bed length : 12.5 cm

Particle size : 28/32 mesh

Table III.4 - Retention times of pyridine in H-mordenite.
(Injection volume: 1 μ L)

Operational conditions: 100°C; 15 cc/min (He).

Inlet pulse (min)	Retention time (min)	Area: Inlet peak (counts)	Area: Response signal (counts)
0.28	1.13	3.44×10^6	1.56×10^6 (46%)
0.28	1.07	3.43×10^6	1.67×10^6 (49%)
0.28	1.03	3.40×10^6	1.67×10^6 (49%)
0.28	1.23	3.32×10^6	2.32×10^6 (69%)

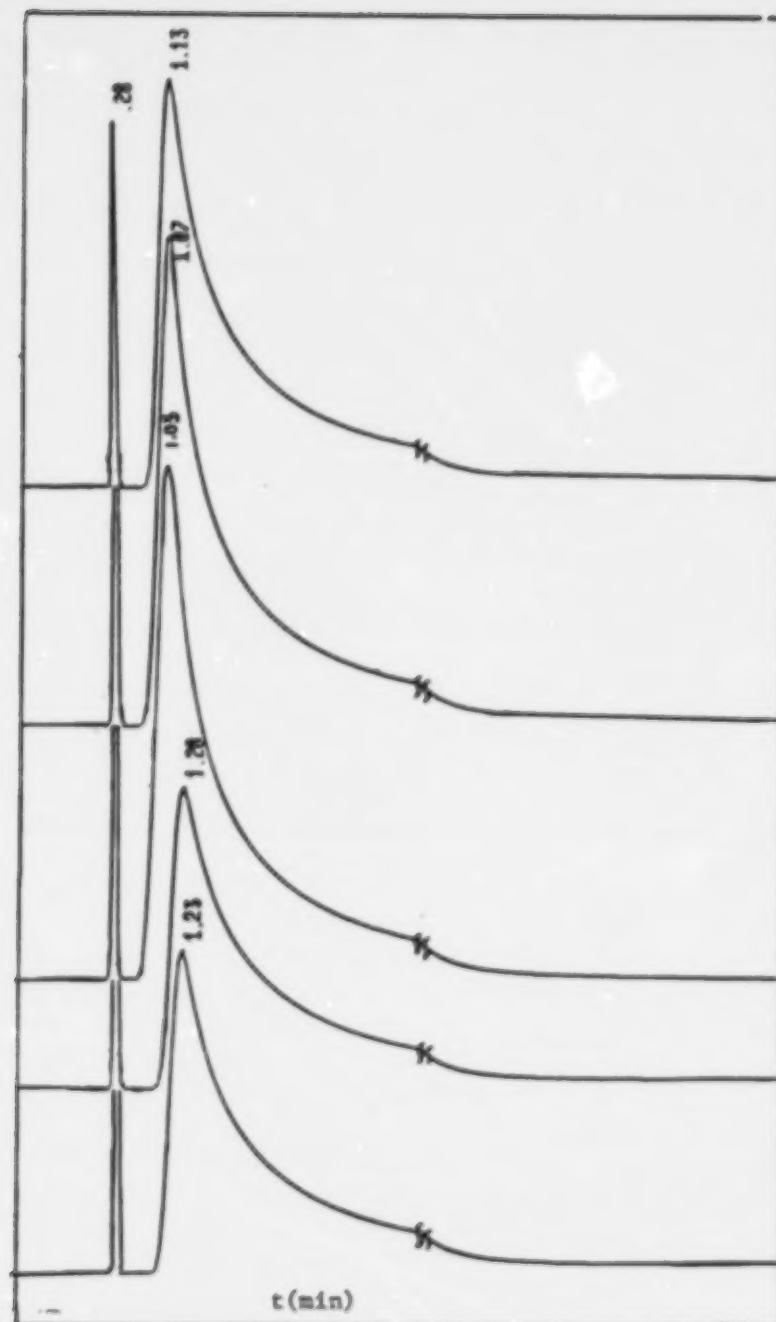


Figure III.3. Experimental chromatograms for the pyridine/H-mordenite system (15 cc/min; 100°C; 1 μ L).

Table III.5 - Retention times of pyridine in H-mordenite.
(Injection volume: 1 μ L) (Fig. III.4)

Operational conditions: 100°C; 45 cc/min (He).

Inlet pulse (min)	Retention time (min)	Area: Inlet pulse (counts)	Area: Response signal (counts)
0.09	0.85	1.10×10^6	1.80×10^5 (17%)
0.10	0.58	1.10×10^6	1.70×10^5 (15%)
0.10	0.52	1.10×10^6	1.20×10^5 (11%)
0.09	0.57	1.11×10^6	4.60×10^5 (41%)
0.09	0.93	1.10×10^6	2.14×10^5 (20%)
0.09	0.85	1.10×10^6	4.56×10^5 (41%)
0.10	0.79	1.10×10^6	5.37×10^5 (49%)
0.09	0.75	1.10×10^6	4.16×10^5 (38%)
0.10	0.70	1.10×10^6	4.67×10^5 (43%)

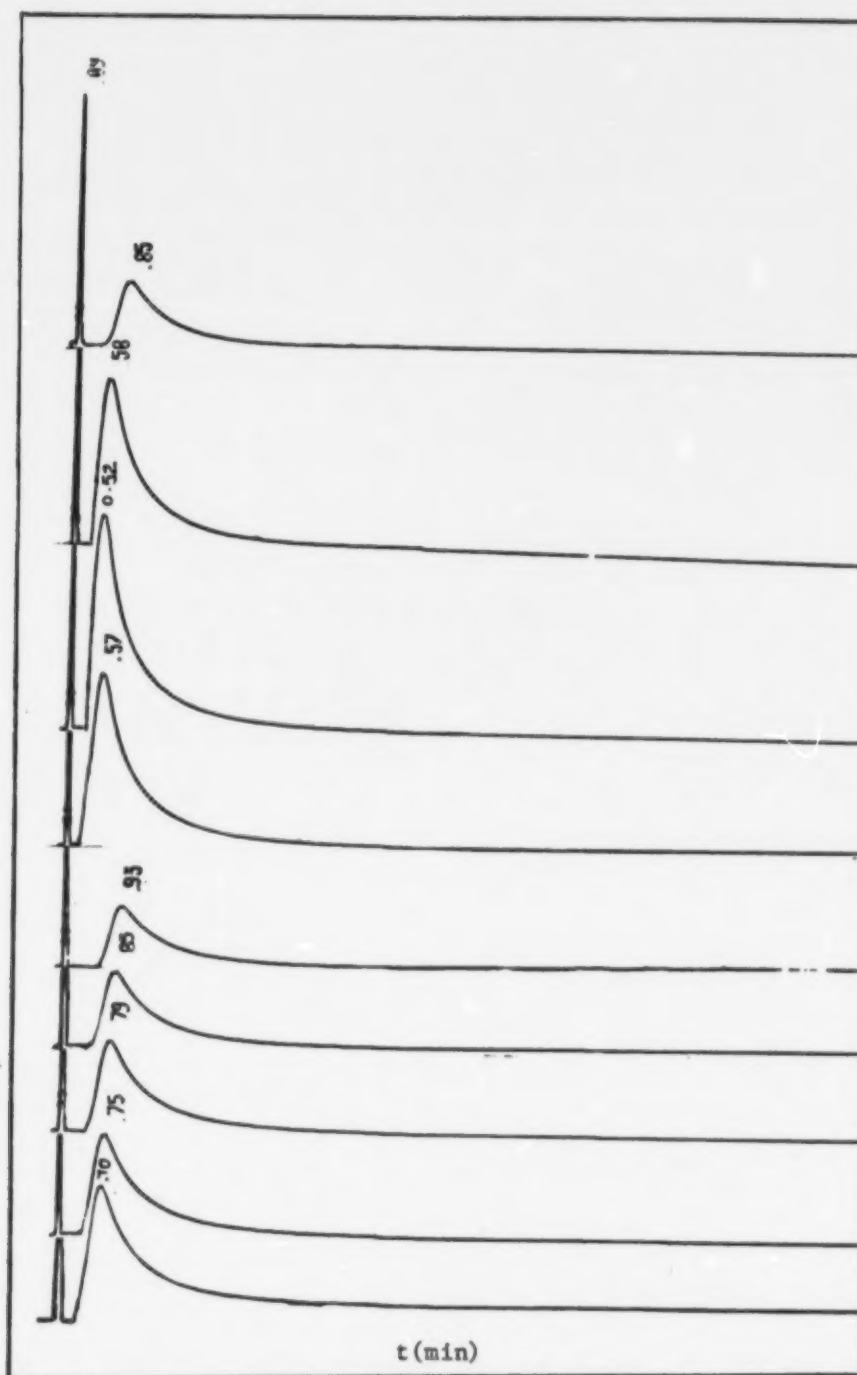


Figure III.4. Experimental chromatograms for the pyridine/H-mordenite system (45 cc/min; 100°C; 1 μ L).

Table III.6 - Retention times of pyridine in H-mordenite.
(Injection volume: 1 μ L) (Fig. III.5)

Operational conditions: 125°C; 30 cc/min (He).

Inlet pulse (min)	Retention time (min)	Area: Input pulse (counts)	Area: Response signal (counts)
0.13	0.67	1.67×10^6	8.69×10^5 (52%)
0.13	0.67	1.67×10^6	- (?)*
0.13	0.73	1.67×10^6	- (?)
0.13	0.66	1.67×10^6	- (?)
0.13	0.61	1.67×10^6	- (?)
0.13	0.68	1.66×10^6	- (?)

* Integrator malfunctioned.

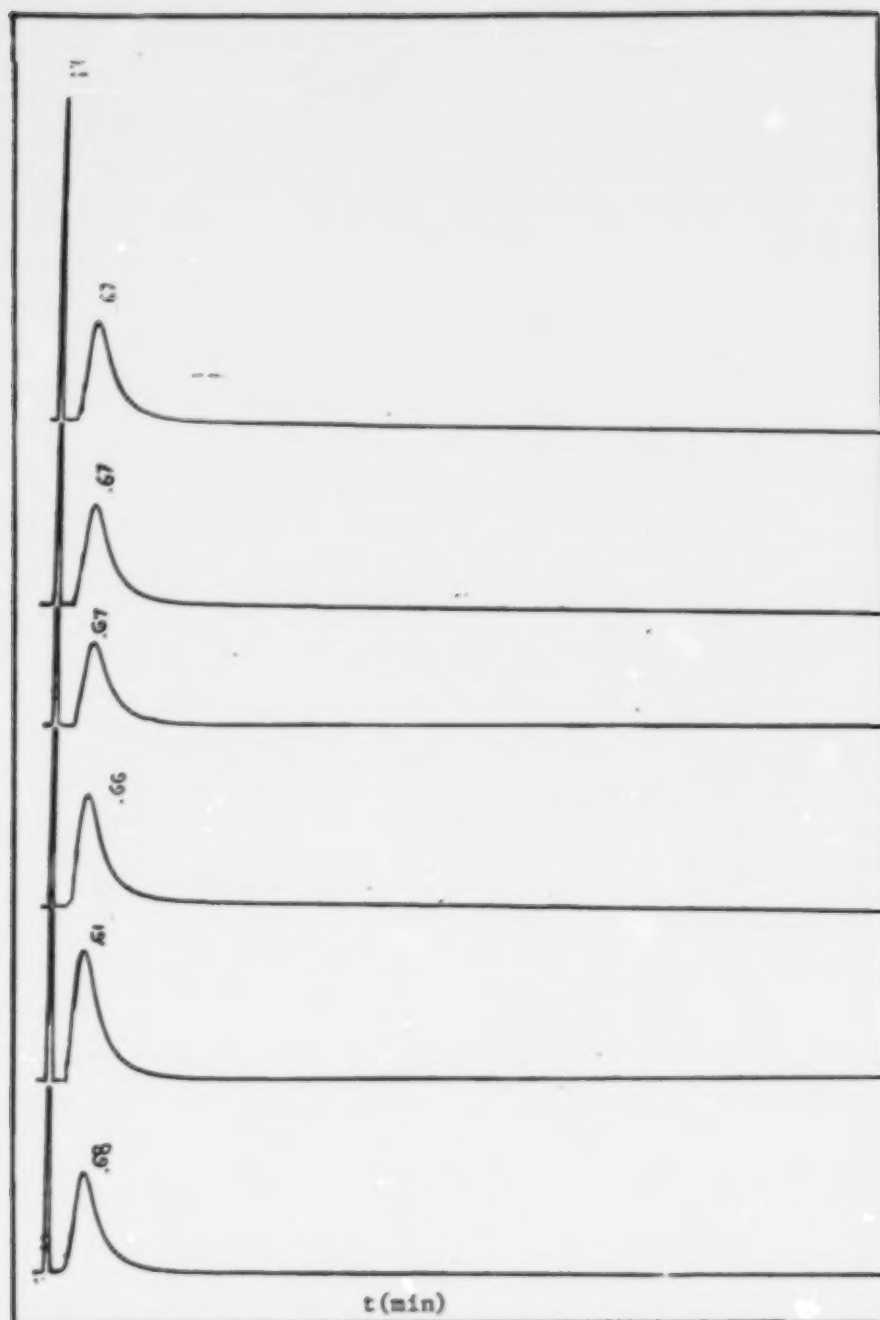


Figure III.5. Experimental chromatograms for the pyridine/H-mordenite system (30 cc/min; 125°C; 1 μ L).

Table III.7 - Retention times of pyridine in H-mordenite.
(Injection volume: 1 μ L) (Fig. III.6)

Operational conditions: 150°C; 30 cc/min (He).

Inlet pulse (min)	Retention time (min)	Area: Inlet pulse (counts)	Area: Response signal (counts)
0.11	0.31	1.68×10^6	5.22×10^5 (31%)
0.11	0.30	1.68×10^6	5.53×10^5 (33%)
0.11	0.31	1.63×10^6	5.89×10^5 (36%)
0.11	0.30	1.63×10^6	0.43×10^5 (39%)
0.12	0.33	1.66×10^6	8.36×10^5 (51%)
0.12	0.31	1.67×10^6	6.79×10^5 (41%)

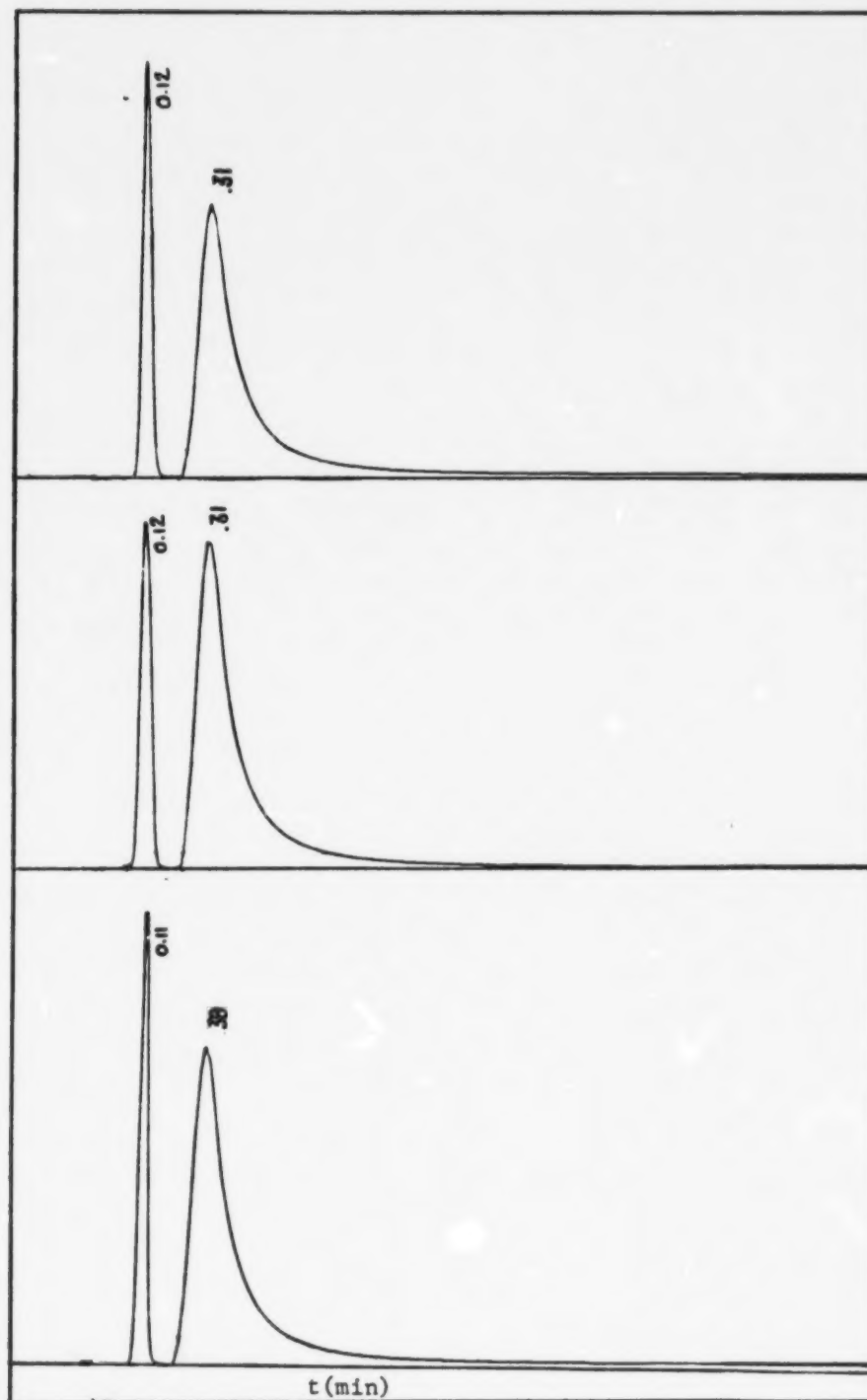


Figure III.6. Experimental chromatograms for the pyridine/H-mordenite system (30 cc/min; 150°C; 1 μ L).

temperature increased the elution time for the pyridine peak maxima which was accompanied by a broadening of the response peak signal (figs. III.7-III.11). The extreme sensitivity of the response signal to temperature can be seen clearly in figure III.11. At 150°C (He flow rate: 30 cc/min) the signal has virtually broadened into the background. This behaviour is exactly the opposite to what is observed with the pyridine/H-mordenite system.

III.2.4 Pyridine/Ca-mordenite system

Results obtained for this system are reported in tables III.13-III.15 and in figures III.12 - III.14. The system is nonlinear under the conditions of operation. The effect of the injection volume on the response signal can be clearly seen in tables III.14, III.15 and also in figures III.13, III.14. A decrease in the injection volume caused an increase in the elution time for pyridine indicating the nonlinear behaviour of the system. The temperature effect on this system is similar to what is observed with the pyridine/H-mordenite system. Tables III.13 - III.15 and figures III.12-III.14 show that an increase in temperature causes a decrease in elution times for pyridine. This behaviour is opposite to the observed behaviour of the pyridine/Na-mordenite system for similar temperature increases.

In general the data obtained with the pyridine/Ca-mordenite system exhibit better reproducibility, and the tailing of the response signal is less pronounced than with the other systems described. However, the tailing becomes significant at low injection volumes (see figs. III.13, III.14).

System: Pyridine/Na-mordenite (Fig. III.7)

Bed parameters:

Weight of adsorbent : 1.45

Packed bed length : 11.5 cm

Particle size : 28/32 mesh

Table III.8 - Retention times of pyridine in Na-mordenite.
(Injection volume: 1 μ L)

Operational conditions: 100°C; 15 cc/min (He).

Inlet pulse (min)	Retention time (min)	Area: Inlet pulse (counts)	Area: Response signal (counts)
0.27	5.99	3.30×10^6	3.80×10^6
0.28	12.38	3.32×10^6	2.38×10^6
0.28	11.50	3.31×10^6	1.52×10^6

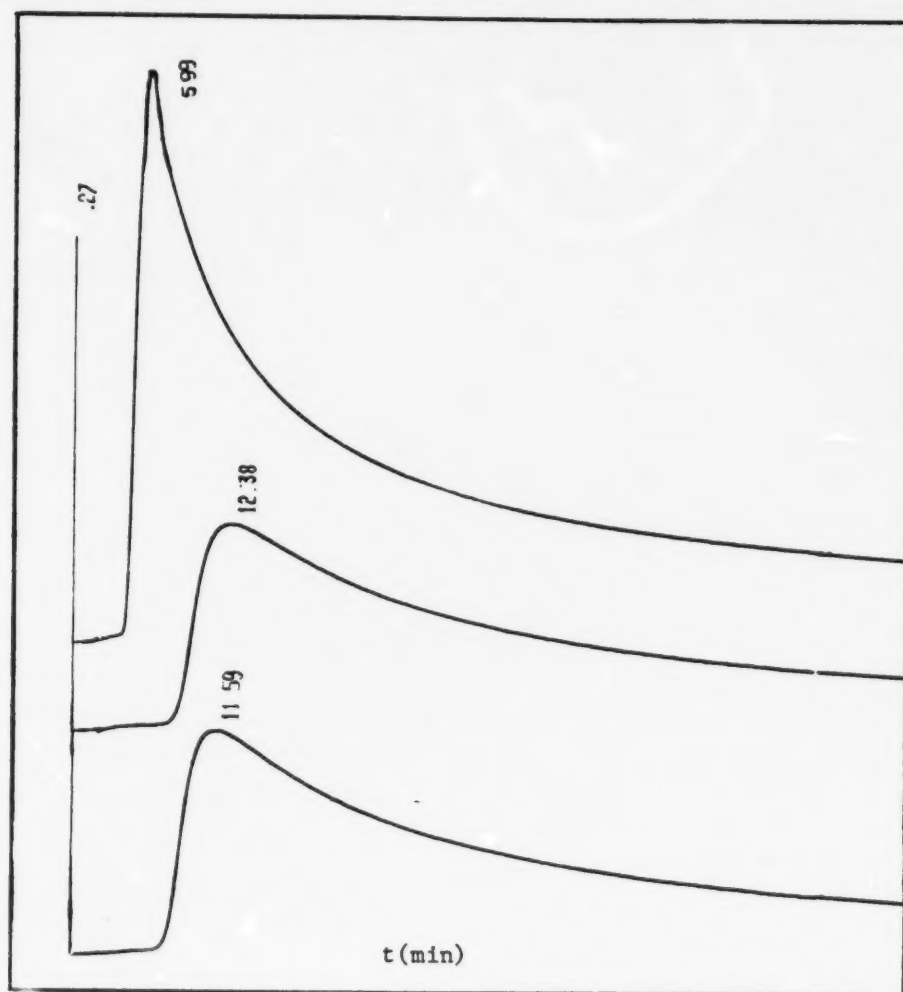


Figure III.7. Experimental chromatograms for the pyridine/Na-mordenite system (15 cc/min; 100°C; 1 μ L).

Table III.9 - Retention times of pyridine in Na-mordenite.
(Injection volume: 1 μ L) (Fig. III.8)

Operational conditions: 100°C; 30 cc/min (He).

Run	Inlet pulse (min)	Retention time (min)	Area: Inlet pulse (counts)	Area: Response signal (counts)
A) 1	0.14	74.61	1.58×10^6	4.85×10^4
2	0.14	19.88	1.59×10^6	1.27×10^6
B) 1	0.14	20.52	1.58×10^6	4.79×10^4
2	0.14	7.19	1.60×10^6	1.35×10^6
3	0.14	8.01	1.59×10^6	7.33×10^5
C) 1	0.14	3.65	1.55×10^6	9.56×10^4
2	0.14	2.08	1.60×10^6	9.52×10^4
3	0.14	2.38	1.60×10^6	1.04×10^5
4	0.14	9.82	1.57×10^6	9.80×10^4
5	0.14	10.47	1.61×10^6	9.79×10^4
6	0.14	7.20	1.61×10^6	1.18×10^5

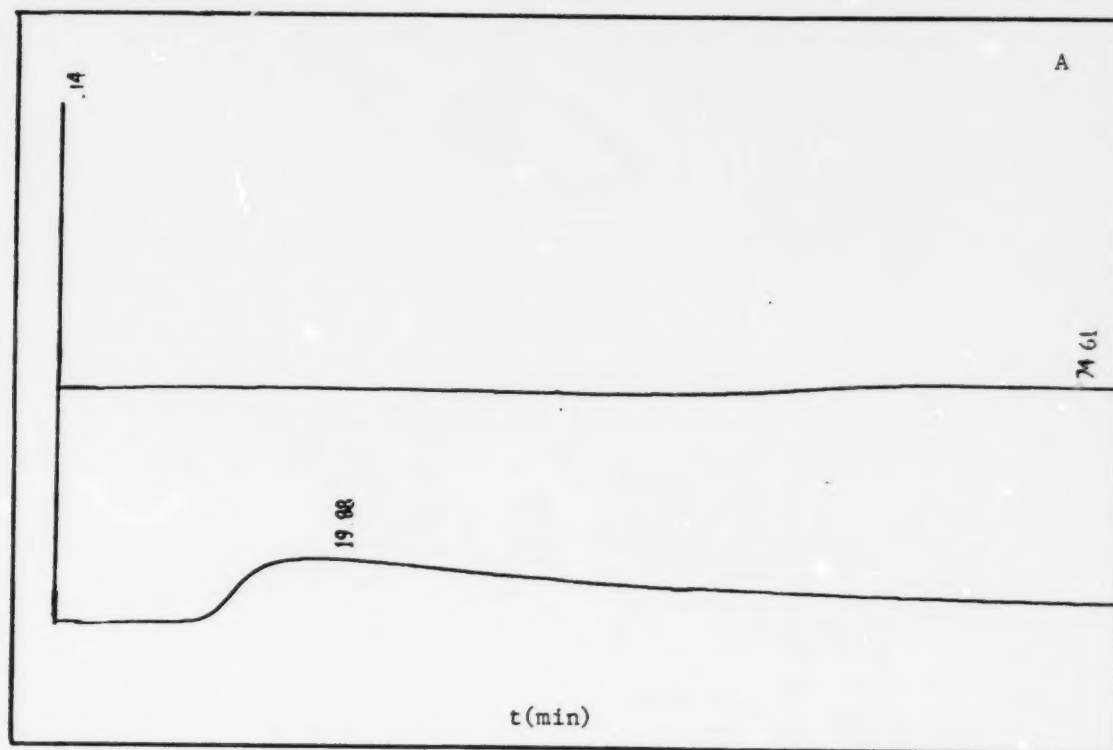


Figure III.8. Experimental chromatograms for the pyridine/Na-mordenite system (30 cc/min; 100°C; 1 μ L).

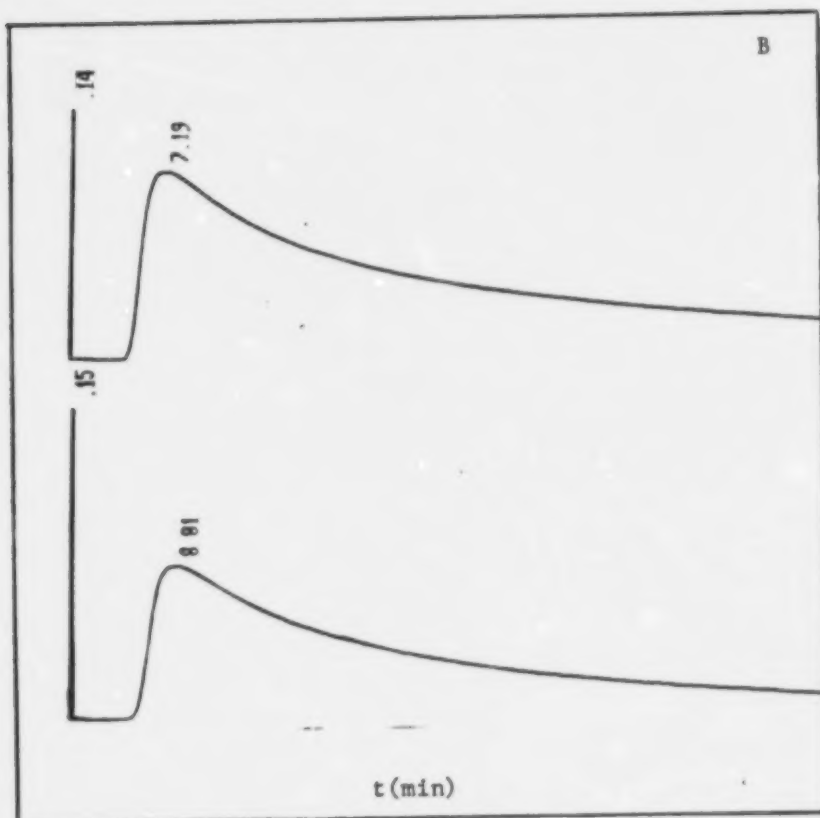


Figure III.8. (Continued)

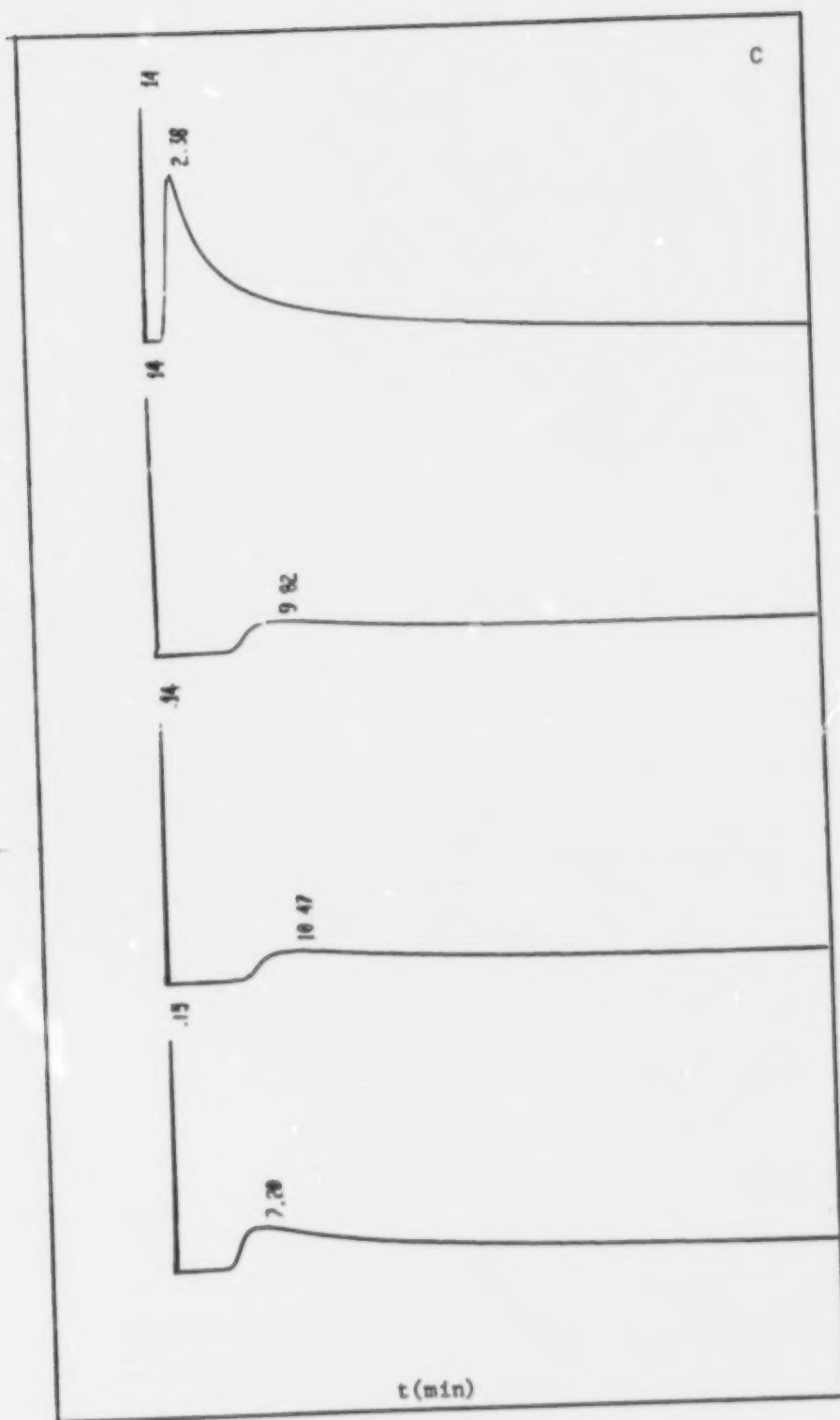


Figure III.8. (Continued)

Table III.10 - Retention times of pyridine in Na-mordenite.
(Injection volume: 1 μ L) (Fig. III.9)

Operational conditions: 100°C; 45 cc/min (He).

Inlet pulse (min)	Retention time (min)	Area: Inlet pulse (counts)	Area: Response signal (counts)
0.09	12.08	1.09×10^4	4.30×10^4
0.09	14.07	1.09×10^4	-

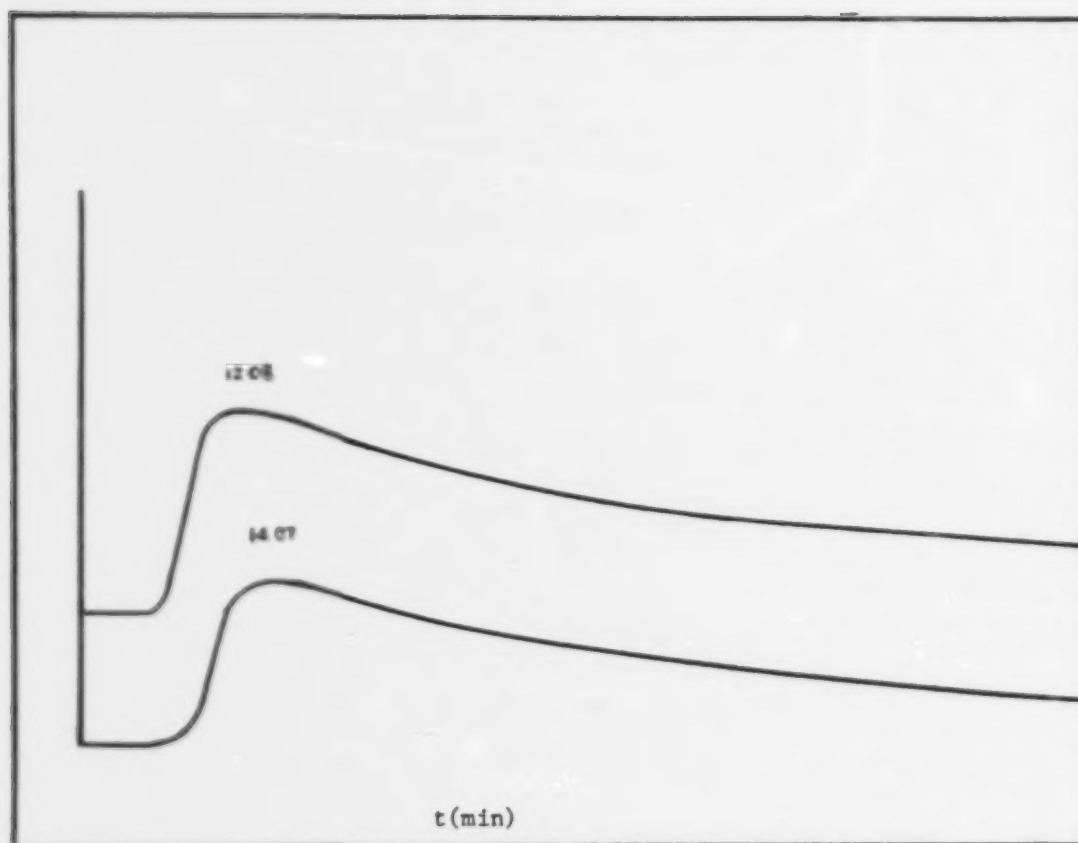


Figure III.9. Experimental chromatograms for the pyridine/Na-mordenite system (45 cc/min; 100°C; 1 μL).

Table III.11 - Retention times of pyridine in Na-mordenite.
(Injection volume: 1 μ L) (Fig. III.10)

Operational conditions: 125°C; 30 cc/min (He).

Inlet pulse (min)	Retention time (min)	Area: Input pulse (counts)	Area: Response signal (counts)
0.12	6.07	1.60×10^6	7.93×10^5
0.13	38.09	1.60×10^6	4.73×10^5
0.13	33.76	1.63×10^6	5.99×10^5

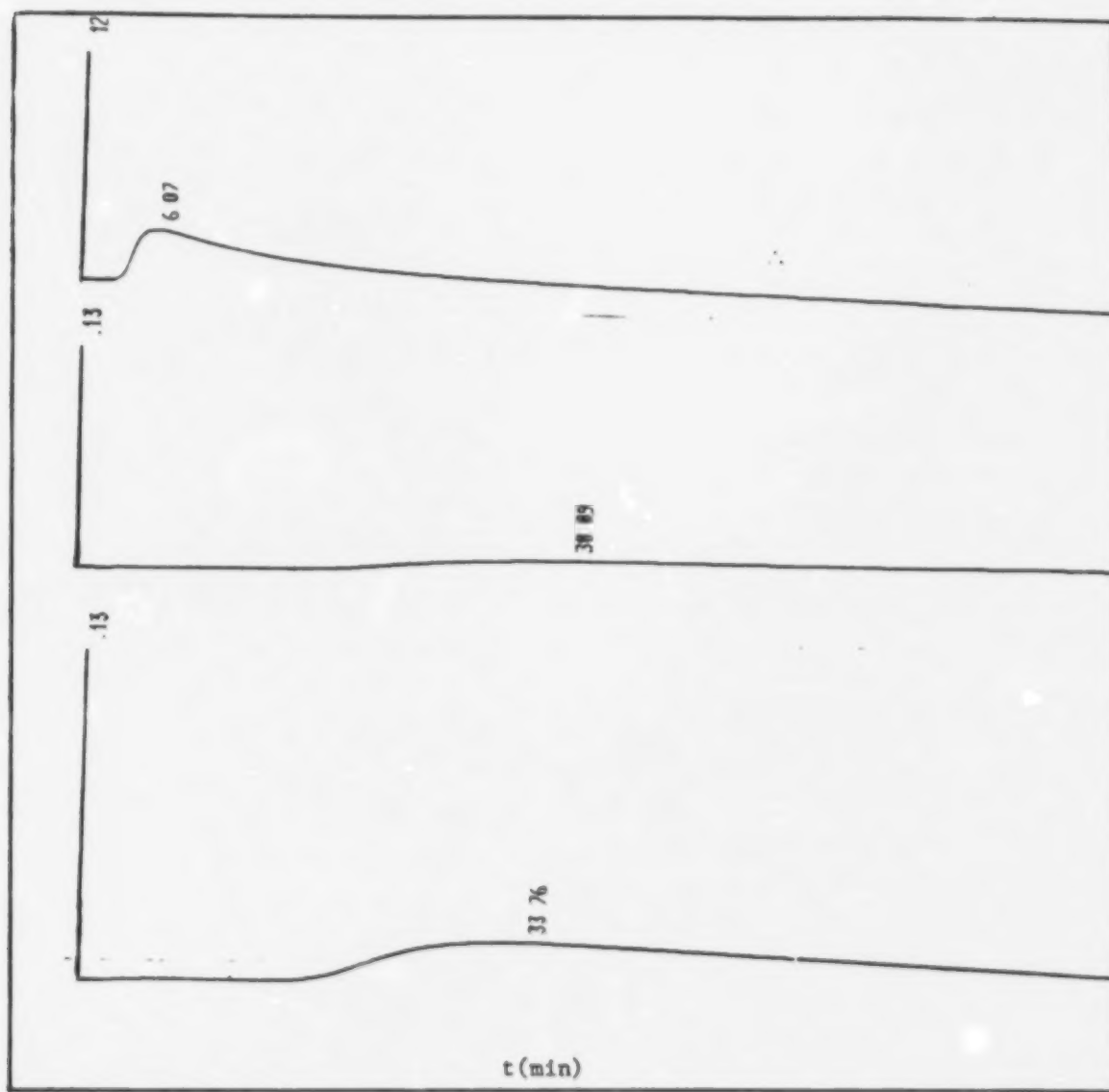


Figure III.10. Experimental chromatograms for the pyridine/Na-mordenite system (30 cc/min; 125°C; 1 μ L).

Table III.12 - Retention times of pyridine in Na-mordenite.
(Injection volume: 1 μ L) (Fig. III.11)

Operational conditions: 150°C; 30 cc/min (He).

Inlet pulse (min)	Retention time (min)	Area: Inlet pulse (counts)	Area: Response pulse (counts)
0.12	21.6	1.62×10^6	5.22×10^5
0.12	44.23	1.68×10^6	5.07×10^5
0.12	44.65	1.66×10^6	5.15×10^5

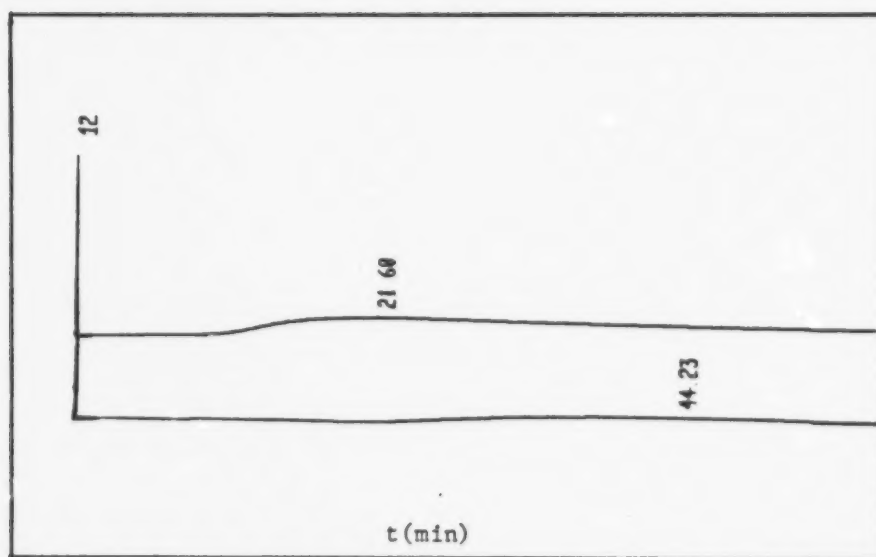


Figure III.11. Experimental chromatograms for the pyridine/Na-mordenite system (30 cc/min; 150°C; 1 μ L).

System: Pyridine/Ca-mordenite (Fig. III.12)

Bed parameters:

Weight of adsorbent : 1.28 g
 Packed bed length : 11.5 cm
 Particle size : 28/32 mesh

Table III.13 - Retention times of pyridine in Ca-mordenite.
 (Injection volume: 1 μ L)

Operational conditions: 100°C; 30 cc/min (He).

Inlet pulse (min)	Retention time (min)	Area: Inlet pulse (counts)	Area: Response signal (counts)
0.07	3.72	1.64×10^6	1.73×10^5
0.07	1.73	1.64×10^6	4.35×10^5
0.07	2.51	1.64×10^6	4.39×10^5
0.07	1.20	1.64×10^6	5.94×10^5
0.07	1.08	1.64×10^6	6.33×10^5
0.07	1.03	1.64×10^6	6.55×10^5
0.07	1.06	1.64×10^6	6.48×10^5
0.07	0.99	1.64×10^6	6.77×10^5

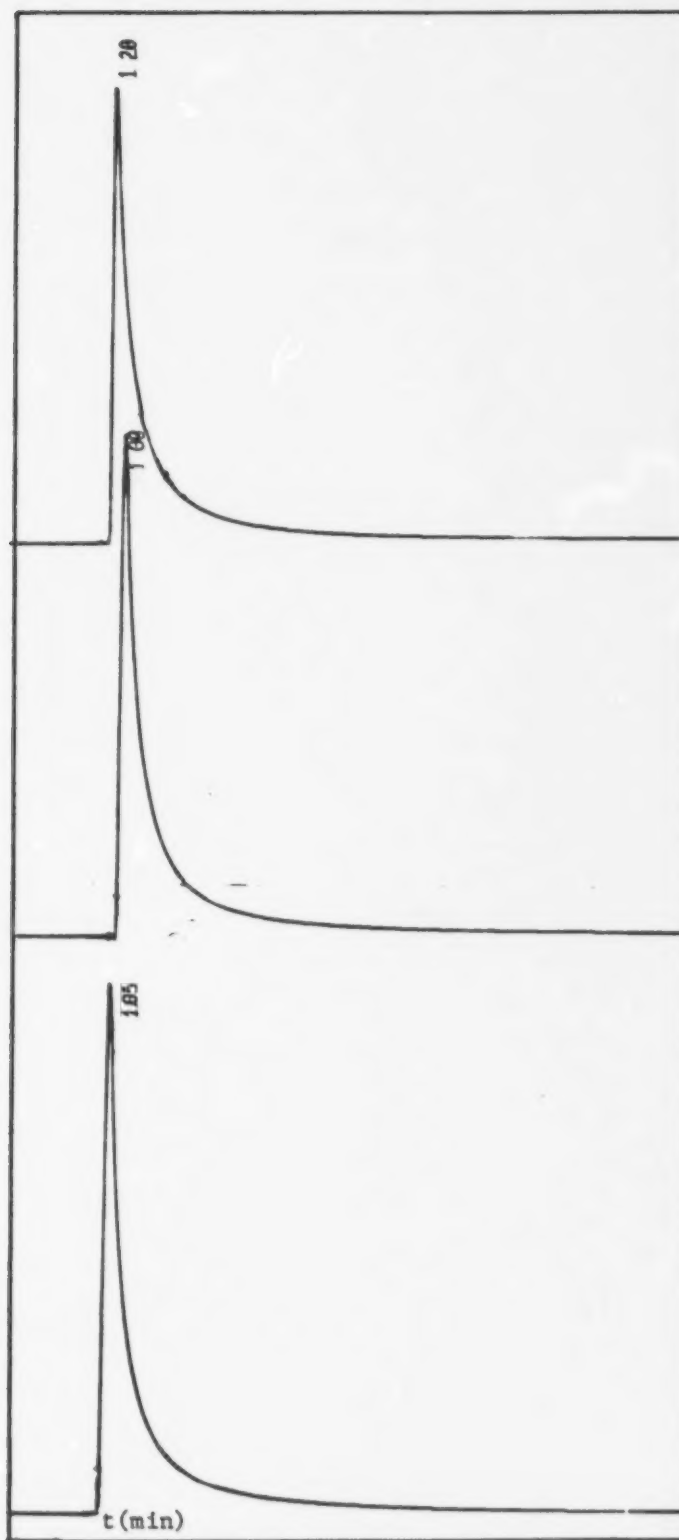


Figure III.12. Experimental chromatograms for the pyridine/Ca-mordenite system (30 cc/min; 100°C; 1 μ L).

Table III.14 - Retention times of pyridine in Ca-mordenite.
(Injection volume: 1 μ L) (Fig. III.13)

Operational conditions: 125°C; 30 cc/min (He).

Inlet pulse (min)	Retention time (min)	Area: Inlet pulse (counts)	Area: Response signal (counts)
A			
0.06	0.91	1.65×10^6	2.69×10^5
0.06	0.98	1.65×10^6	2.43×10^5
0.06	0.86	1.65×10^6	3.15×10^5
0.06	0.77	1.65×10^6	3.87×10^5
0.06	0.67	1.65×10^6	4.73×10^5
0.06	0.65	1.65×10^6	5.02×10^5
B			
0.06	0.58	1.65×10^6	5.89×10^5
0.06	0.57	1.65×10^6	6.25×10^5
0.06	0.54	1.65×10^6	6.59×10^5
0.06	0.53	1.65×10^6	6.69×10^5
C (Injection volume: 0.5 μ L)			
0.06	2.43	8.19×10^5	1.55×10^5
0.06	2.18	8.19×10^5	1.56×10^5
0.06	2.08	8.19×10^5	1.75×10^5
0.06	2.09	8.19×10^5	1.77×10^5

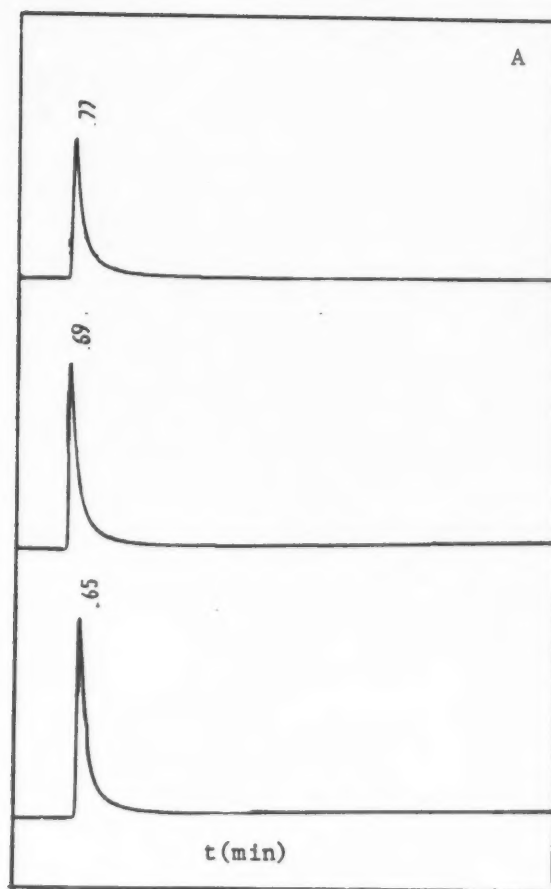


Figure III.13. Experimental chromatograms for the pyridine/Ca-mordenite system (30 cc/min; 125°C; 1 μ L (0.5 μ L)).

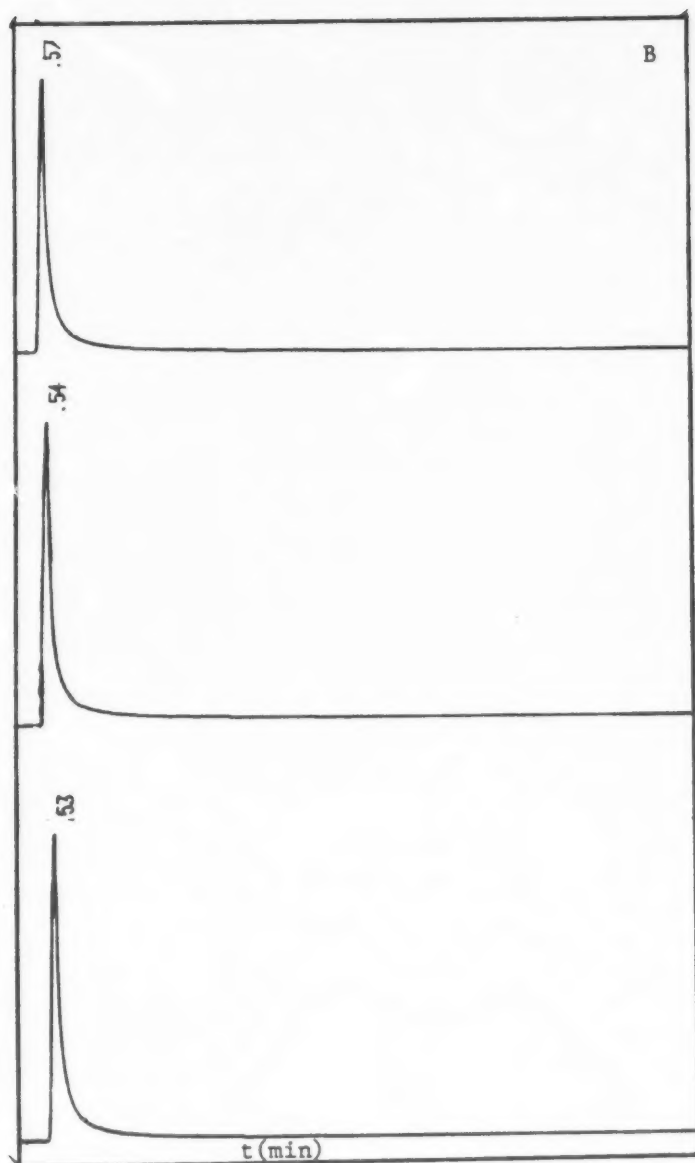


Figure III.13. (Continued)

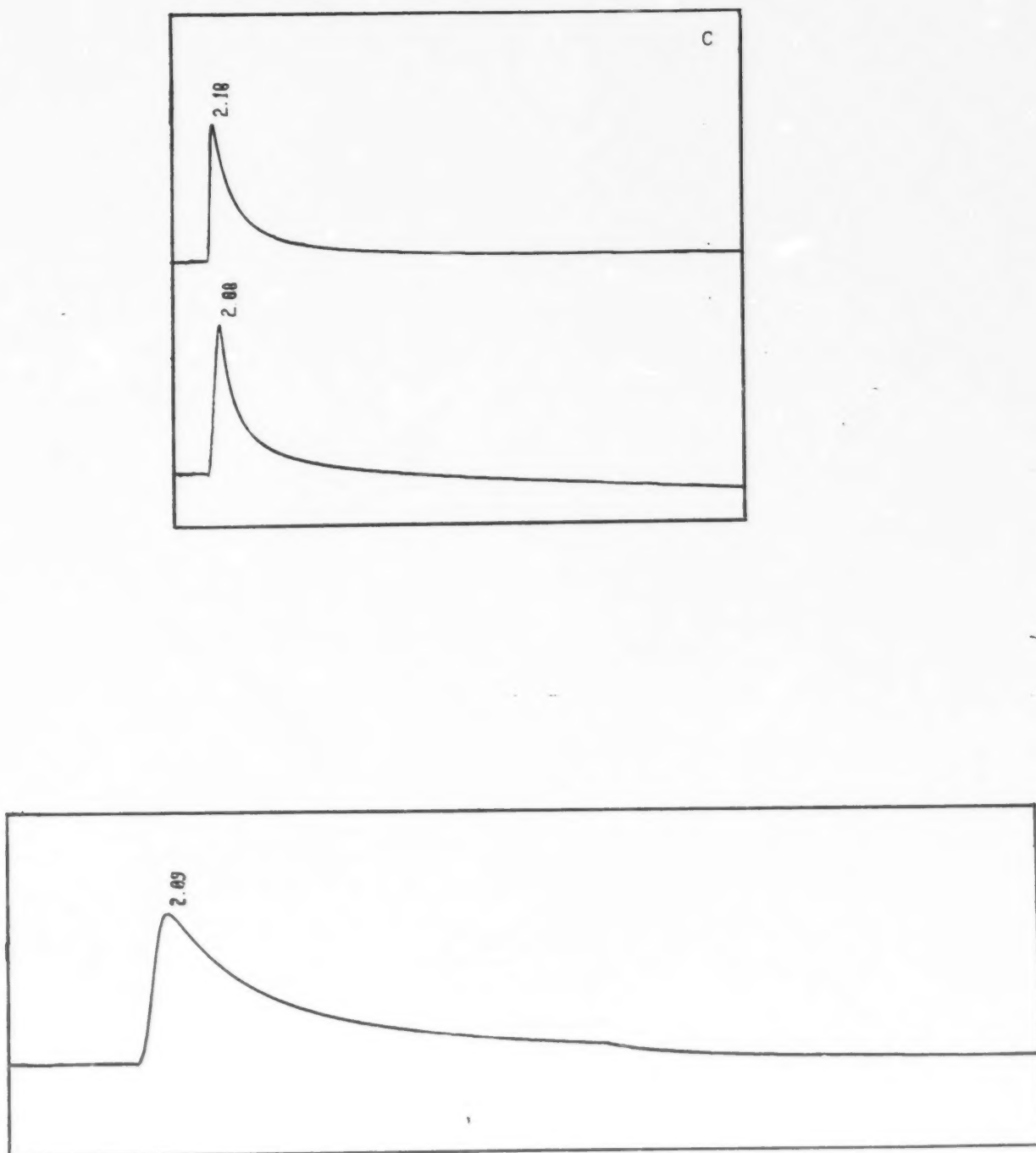


Figure III.13. (Continued)

Table III.15 - Retention times of pyridine in Ca-mordenite. (Fig. III.14)

Operational conditions: 150°C; 30 cc/min (He).

Inlet pulse (min)	Retention time (min)	Area: Inlet pulse (counts)	Area: Response signal (counts)
(1 μ L pulses)			
0.06	0.51	1.66×10^6	1.93×10^5
0.06	0.47	1.66×10^6	2.41×10^5
0.06	0.40	1.66×10^6	3.38×10^5
0.06	0.37	1.66×10^6	4.12×10^5
0.06	0.35	1.66×10^6	4.73×10^5
0.06	0.34	1.66×10^6	5.21×10^5
0.06	0.33	1.66×10^6	5.64×10^5
0.06	0.30	1.66×10^6	6.51×10^5
0.06	0.29	1.66×10^6	6.74×10^5
0.06	0.28	1.66×10^6	7.23×10^5
0.06	0.30	1.66×10^6	7.08×10^5
(0.5 μ L pulses)			
0.06	0.93	8.40×10^5	1.15×10^5
0.06	0.87	8.40×10^5	1.21×10^5

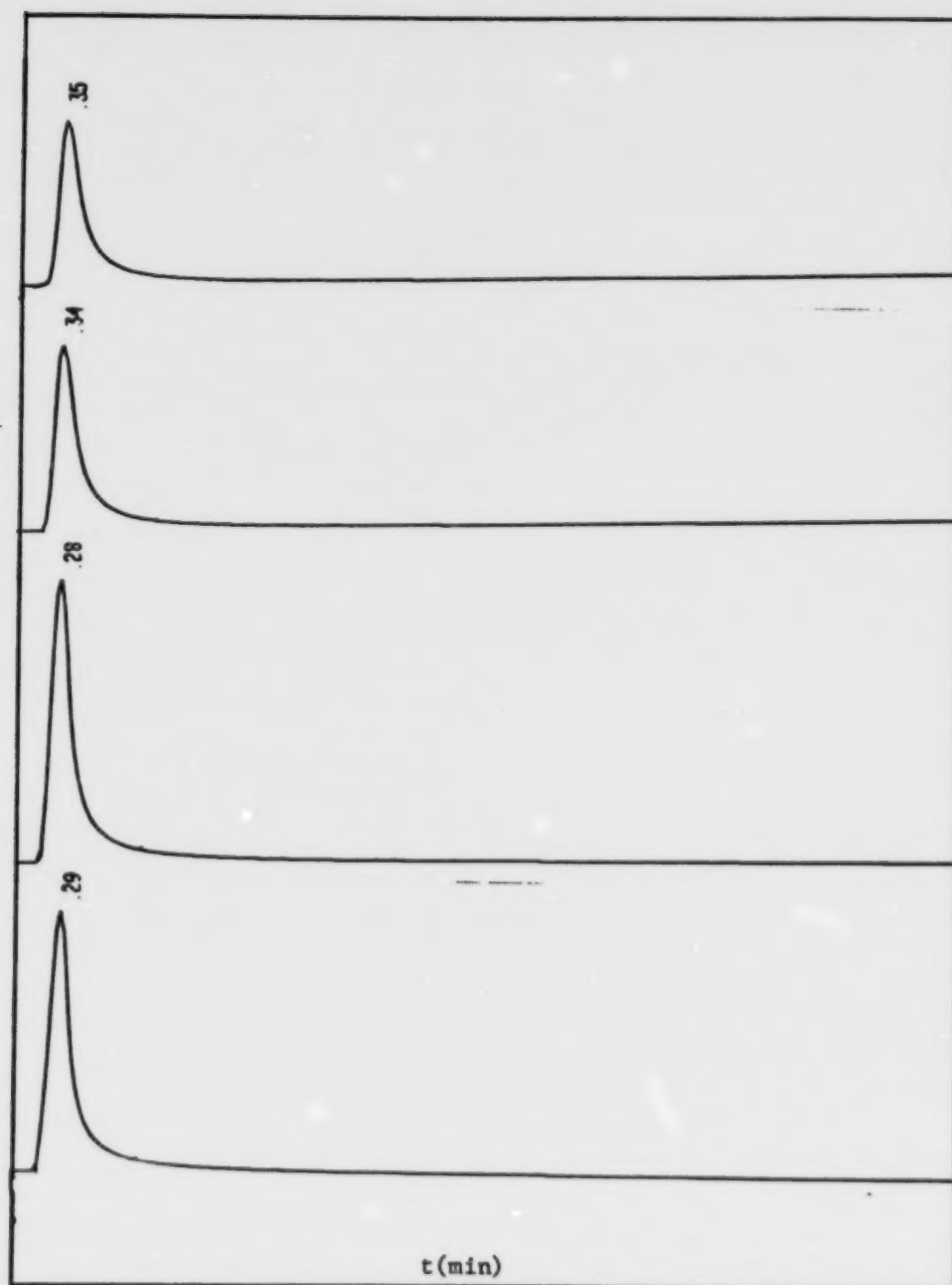


Figure III.14. Experimental chromatograms for the pyridine/Ca-mordenite system (30 cc/min; 150°C; 1 μ L (0.5 μ L)).

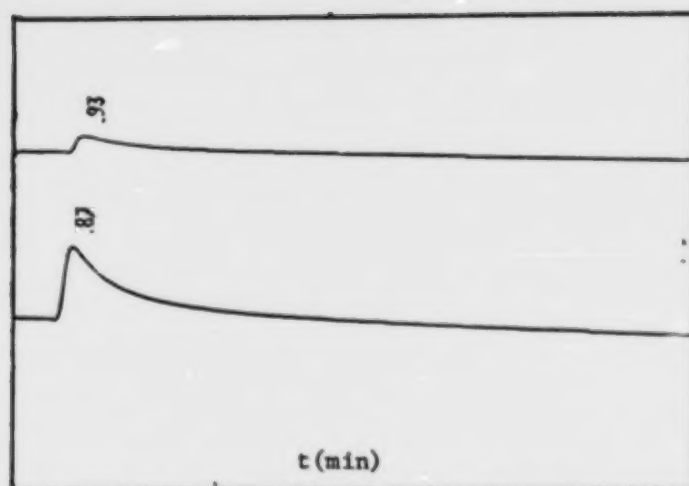


Figure III.14. (Continued)

III.2.5 Pyridine/H-ZSM5 system (Fig. III.15)

Bed parameters:

Weight of adsorbent: 3.59
Packed bed length: 32.9 cm
Particle size: 48/60 mesh

With the pyridine/H-ZSM5 system a reasonable response signal cannot be obtained with low enough injection volumes (fig. III.15). Response signals with very long retention times (in the order of 8-10 hr) characterized by a very long tail are obtained with large injection volumes ($> 4 \mu\text{L}$) and at high temperature (see fig. III.15a, b and d). With injection volumes less than about 4 μL the response signals are broadened into the baseline (fig. III.15c). The response signals obtained with 5 μL injection volumes at 125°C are significantly broader and more dispersed than the signals obtained at 150°C. At 100°C a reasonable signal is not obtained even with an injection volume of 5 μL indicating that the signals have been broadened into the background. Another important observation is the presence of a second broad feature at relatively low retention times on the response signal (fig. III.15a1, b1). This feature is observed with all response signals for this system. The origin of this feature is not yet clear, however it is possible that this stems from a contaminant in the pyridine used.

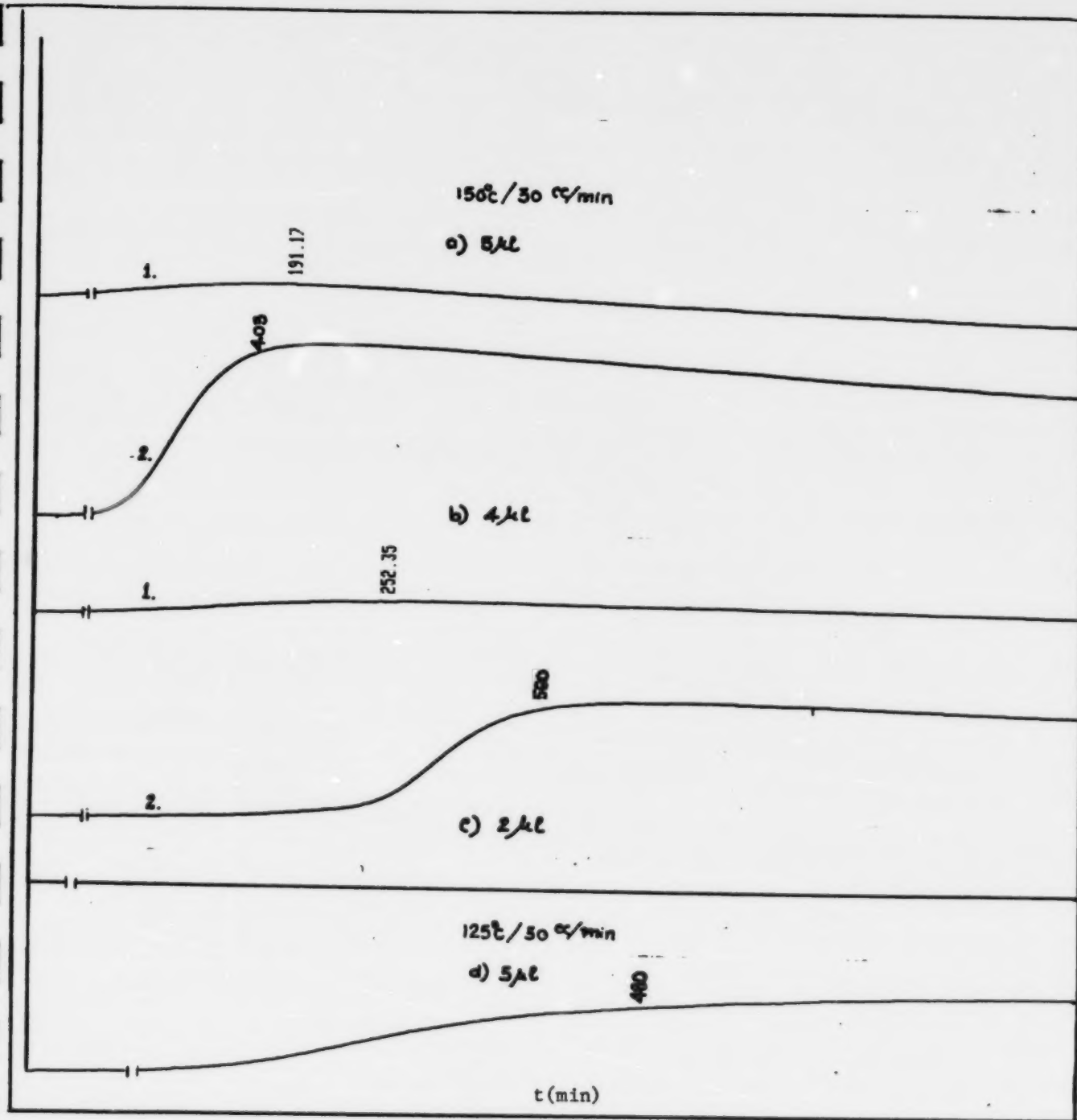


Figure III.15. Experimental chromatograms for the pyridine/H-ZSM5 system.

III.2.6 Pyridine/H-X; pyridine/Na-X; Pyridine/Ca-X systems (Fig. III.16; Fig. III.17)

<u>Bed parameters:</u>	H-X	Na-X	Ca-X
Weight of adsorbent:	0.44	1.0	1.35
Packed bed length:	11.9	11.5	14.2
Particle size:	28/32	28/32	48/60

The behaviour of these three systems are very similar to that of pyridine/H-ZSM5 system. A response signal is obtained only at higher temperatures and with large injection volumes (figs. III.16, III.17). At lower temperatures the response signal is usually broadened into the background.

III.2.7 Pyrrole/H-mordenite, pyrrole/Na-mordenite; Pyrrole/Ca-mordenite systems (Fig. III.18; Fig. III.25)

The results obtained with these systems are given in tables III.16-III.19 and in figures III.18 - III.25. The behaviour of these systems were much more predictable than the corresponding pyridine/zeolite systems. Tailing of the response signals was almost absent except with the pyrrole/Na-mordenite system. With the pyrrole/Na-mordenite system the degree of tailing was greatest at lower temperatures (figs. III.20-III.22). The percentage recovery values given in tables (figures in brackets) are very close to 100% for all systems studied (tables III.16-III.19) except for the pyrrole/Na-mordenite system at low temperatures (table III.18). At these temperatures, the tailing of the response signals is very severe, causing a premature termination of the integration of the response curve resulting in an underestimation of the recovery percentages. Although the behaviour of these systems were nonlinear under the operating

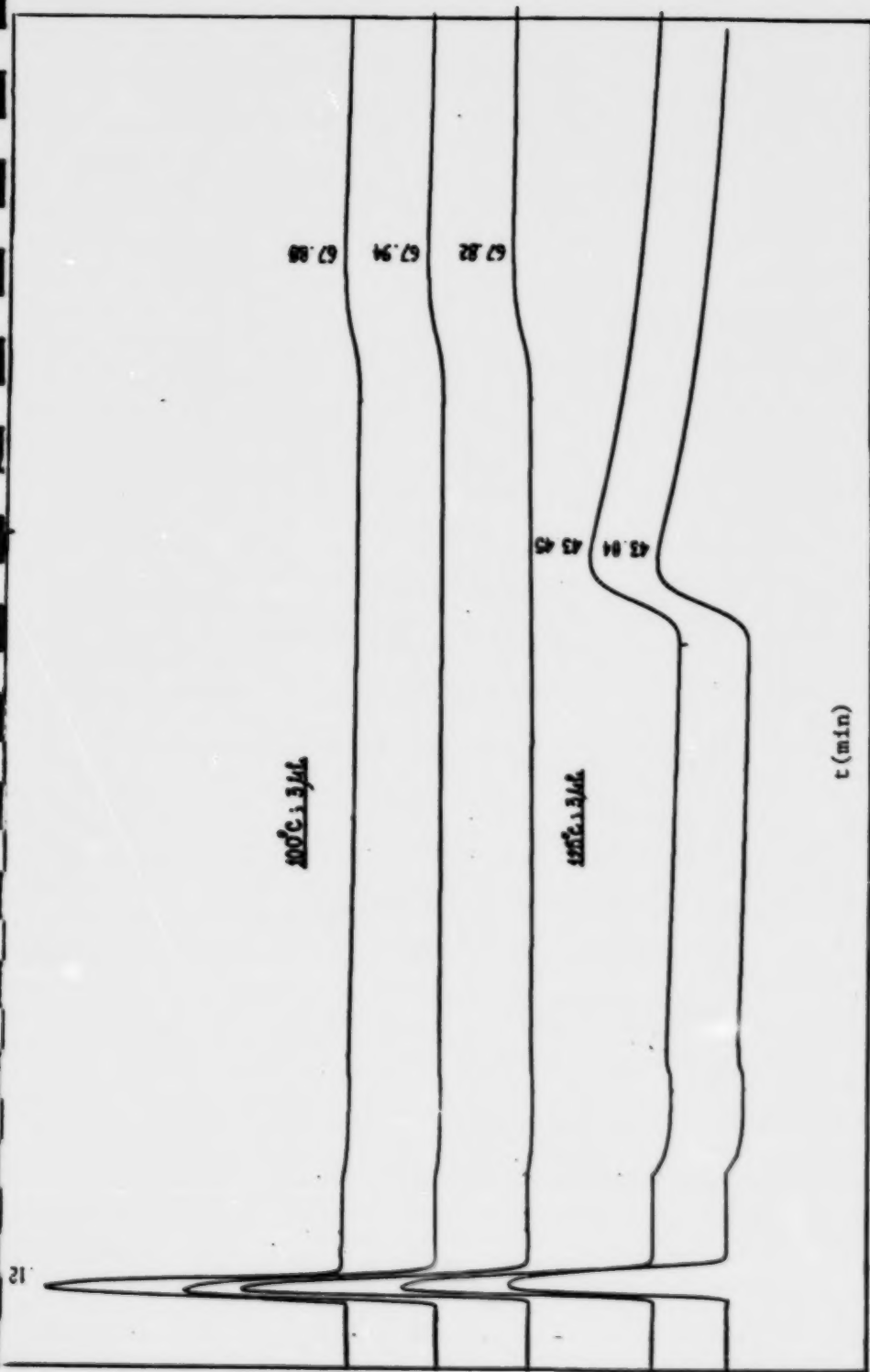


Figure III.16. Experimental chromatograms for the pyridine/H-X system (30 cc/min).

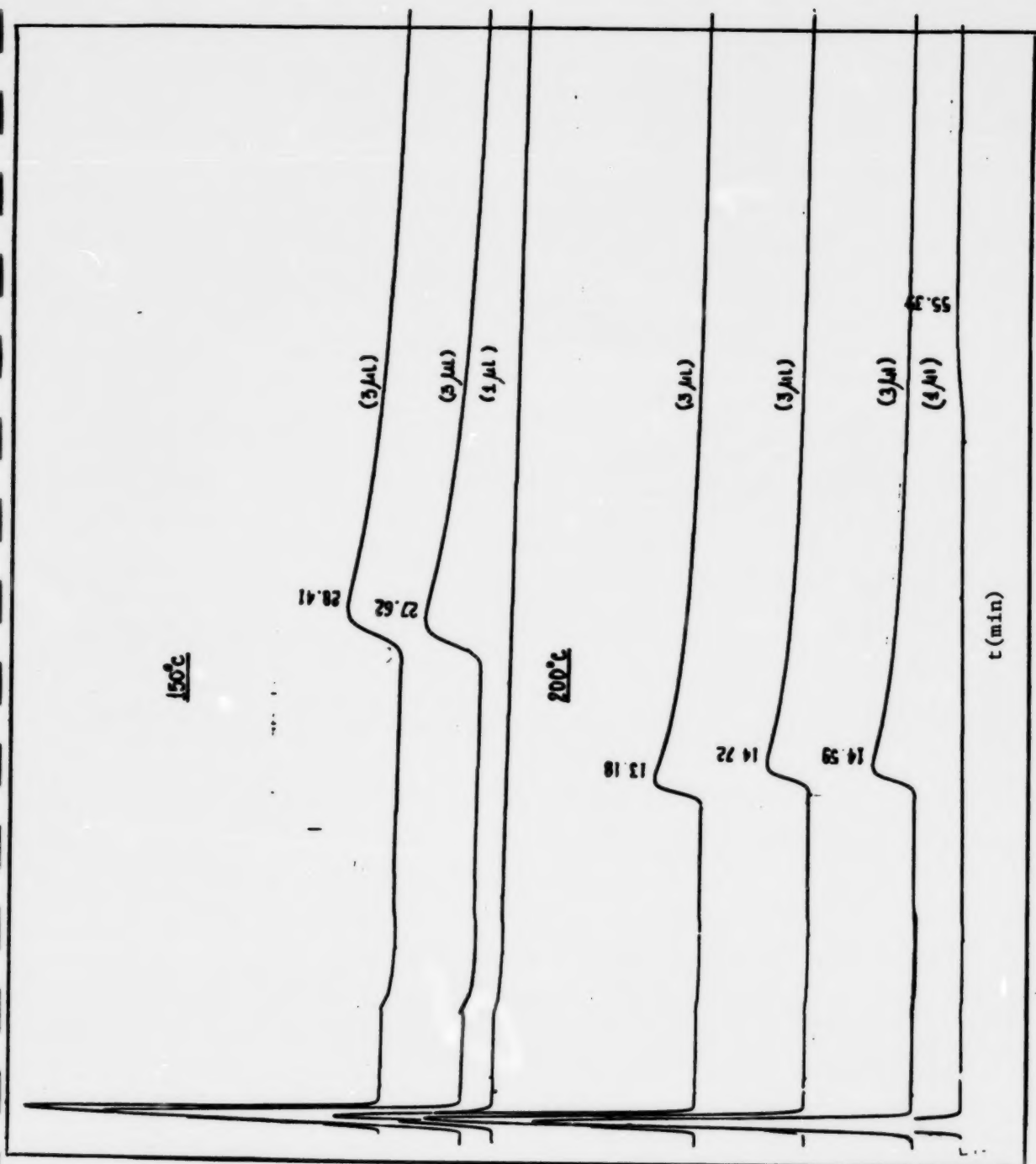


Figure III.16. (Continued)

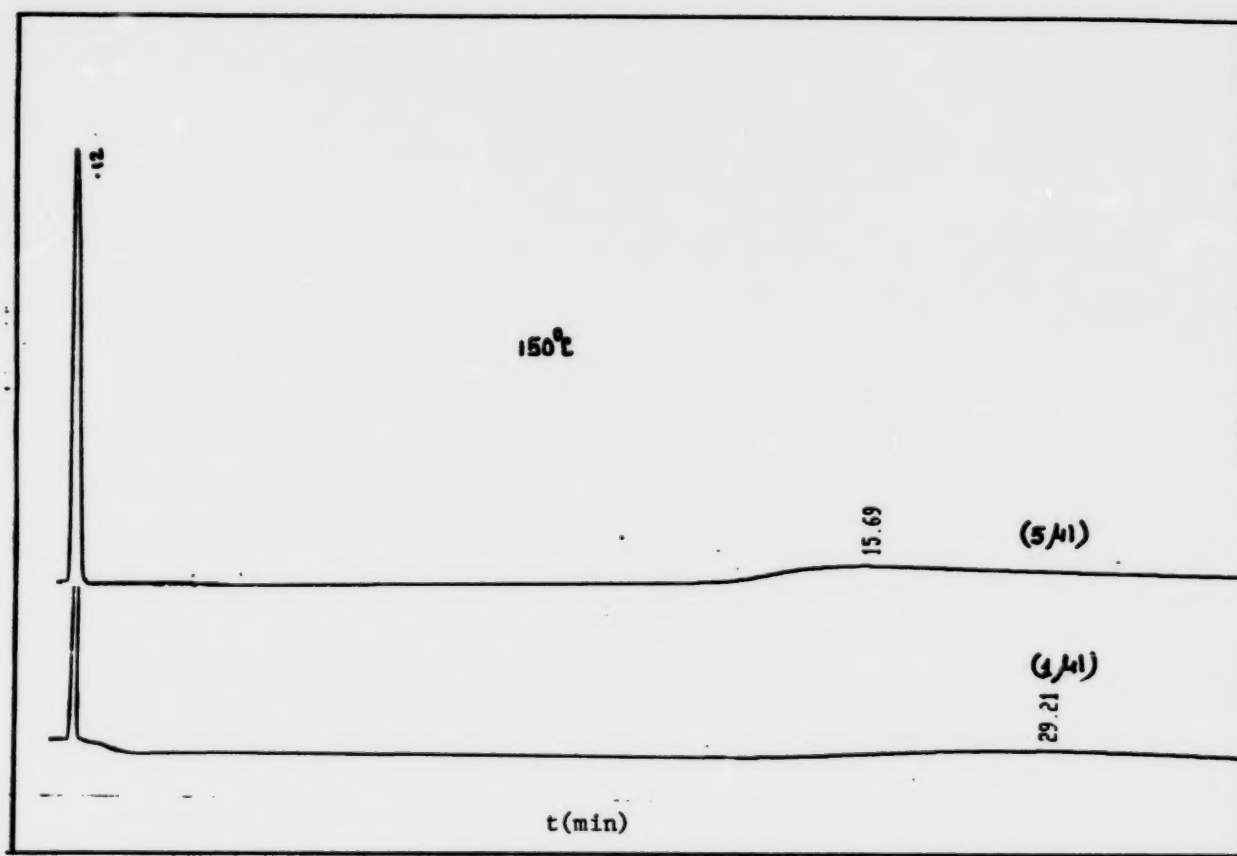


Figure III.17. Experimental chromatograms for the pyridine/Na-X system (30 cc/min).

Bed parameters:

Weight of adsorbent : 1.07 g
 Packed bed length : 9.9 cm
 Particle size : 48/60

Table III.16 - Retention times of pyrrole in H-mordenite.
 (Injection volume: 1 μ L)

Inlet pulse (min)	Retention time (min)	Area: Inlet pulse (counts)	Area: Response signal (counts)
100°C, 30 cc/min			
0.13	0.33	1.90×10^6	1.83×10^6 (96%)
0.13	0.33	1.90×10^6	1.79×10^6 (94%)
0.13	0.31	1.90×10^6	1.83×10^6 (96%)
0.13	0.31	1.90×10^6	1.82×10^6 (95%)
0.13	0.31	1.90×10^6	1.78×10^6 (94%)
125°C, 30 cc/min			
0.13	0.24	1.88×10^6	1.75×10^6 (91%)
0.13	0.24	1.88×10^6	1.81×10^6 (95%)
0.13	0.24	1.88×10^6	1.81×10^6 (95%)
0.13	0.24	1.88×10^6	1.81×10^6 (95%)
0.13	0.24	1.88×10^6	1.83×10^6 (96%)
150°C, 30 cc/min			
0.13	0.21	1.87×10^6	1.90×10^6 (100%)
0.13	0.21	1.87×10^6	1.90×10^6 (100%)
0.13	0.21	1.87×10^6	1.92×10^6 (100%)
0.13	0.21	1.87×10^6	1.90×10^6 (100%)

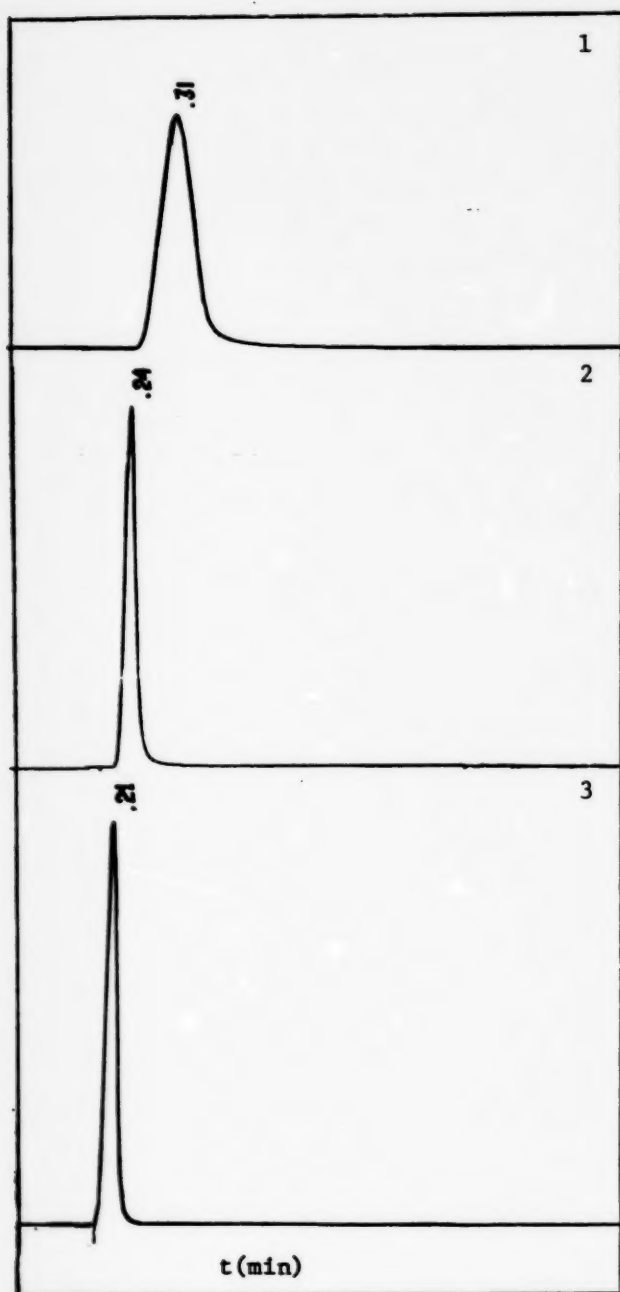


Figure III.18. Experimental chromatograms for the pyrrole/H-mordenite system (30 cc/min; 1 μ L).
1) 100°C; 2) 125°C; 3) 150°C.

System: Pyrrole/H-mordenite (Fig. III.19)

Bed parameters:

Weight of adsorbent : 3.89
 Packed bed length : 32.9 cm
 Particle size : 48/60 mesh

Table III.17 - Retention times of pyrrole in H-mordenite.
 (Injection volume: 1 μ L)

Inlet pulse (min)	Retention time (min)	Area: Inlet pulse (counts)	Area: Response pulse (counts)
100°C, 30 cc/min			
0.13	0.72	1.80×10^6	9.93×10^5 (55%)
0.13	0.71	1.80×10^6	1.46×10^6 (81%)
0.13	0.69	1.80×10^6	1.55×10^6 (86%)
0.13	0.68	1.80×10^6	1.53×10^6 (85%)
125°C, 30 cc/min			
0.12	0.43	1.72×10^6	1.46×10^6 (86%)
0.13	0.41	1.72×10^6	1.57×10^6 (91%)
0.13	0.41	1.72×10^6	1.62×10^6 (94%)
0.12	0.40	1.72×10^6	1.64×10^6 (95%)
0.12	0.41	1.72×10^6	1.62×10^6 (94%)
150°C, 30 cc/min			
0.12	0.32	1.76×10^6	1.48×10^6 (84%)
0.12	0.29	1.76×10^6	1.55×10^6 (88%)
0.12	0.29	1.76×10^6	1.56×10^6 (89%)
0.12	0.30	1.76×10^6	1.49×10^6 (85%)
0.12	0.29	1.76×10^6	1.61×10^6 (91%)
0.12	0.29	1.76×10^6	1.63×10^6 (93%)

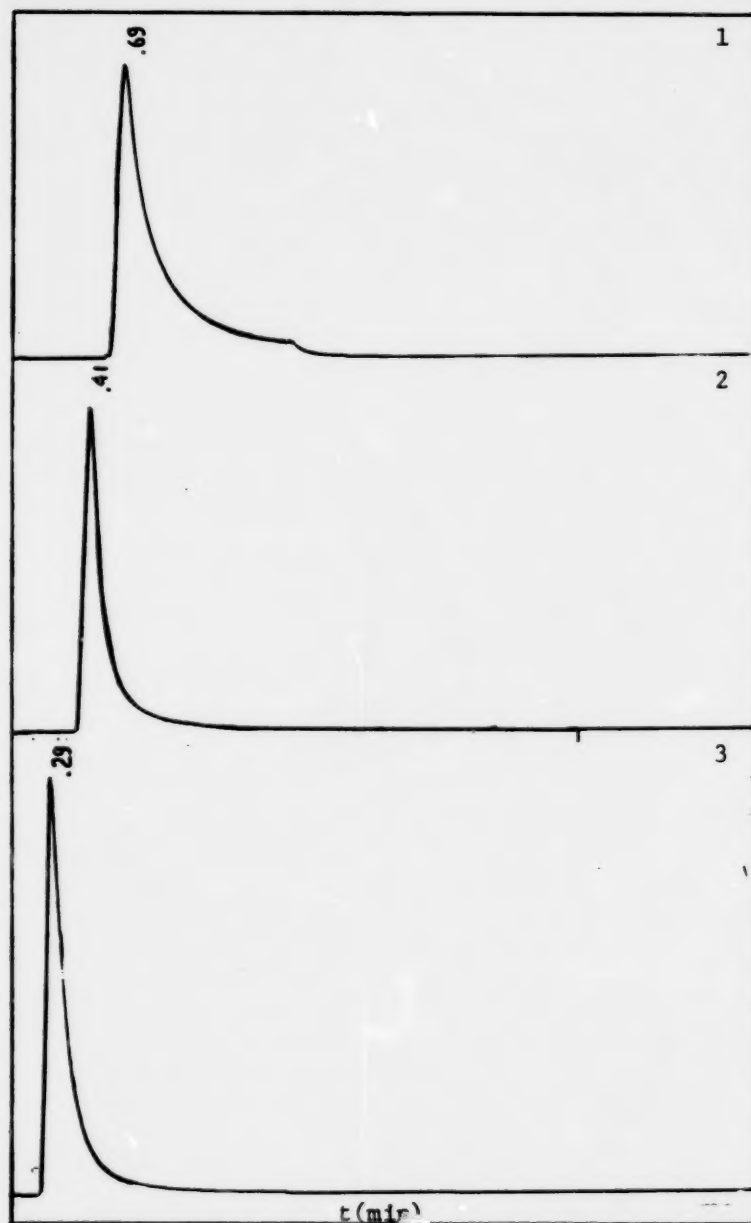


Figure III.19. Experimental chromatograms for the pyrrole/H-mordenite system (30 cc/min; 1 μ L).
1) 100°C; 2) 125°C; 3) 150°C.

System: Pyrrole/Na-mordenite (Fig. III.20 - III.22)

Bed parameters:

Weight of adsorbent : 1.45 g
 Packed bed length : 11.1 cm
 Particle size : 28/32 mesh

Table III.18 - Retention times of pyrrole in Na-mordenite.
 (Injection volume: 1 μ L)

Inlet pulse (min)	Retention time (min)	Area: Inlet pulse (counts)	Area: Response signal (counts)
100°C, 30 cc/min (He)			
0.14	0.87	1.78×10^6	7.37×10^5 (42%)
0.14	0.82	1.78×10^6	7.24×10^5 (41%)
0.14	0.83	1.78×10^6	7.32×10^5 (42%)
0.14	0.79	1.78×10^6	7.54×10^5 (43%)
0.14	0.78	1.78×10^6	7.86×10^5 (45%)
125°C, 30 cc/min (He)			
0.13	0.42	1.77×10^6	9.83×10^5 (56%)
0.13	0.43	1.77×10^6	1.01×10^6 (57%)
0.13	0.41	1.77×10^6	1.05×10^6 (60%)
0.13	0.37	1.77×10^6	1.75×10^6 (99%)
0.13	0.39	1.77×10^6	1.08×10^6 (61%)
0.13	0.41	1.77×10^6	1.09×10^6 (62%)
150°C, 30 cc/min (He)			
0.13	0.28	1.88×10^6	1.75×10^6 (93%)
0.13	0.27	1.88×10^6	1.76×10^6 (94%)
0.13	0.28	1.88×10^6	1.73×10^6 (92%)
0.13	0.28	1.88×10^6	1.73×10^6 (92%)

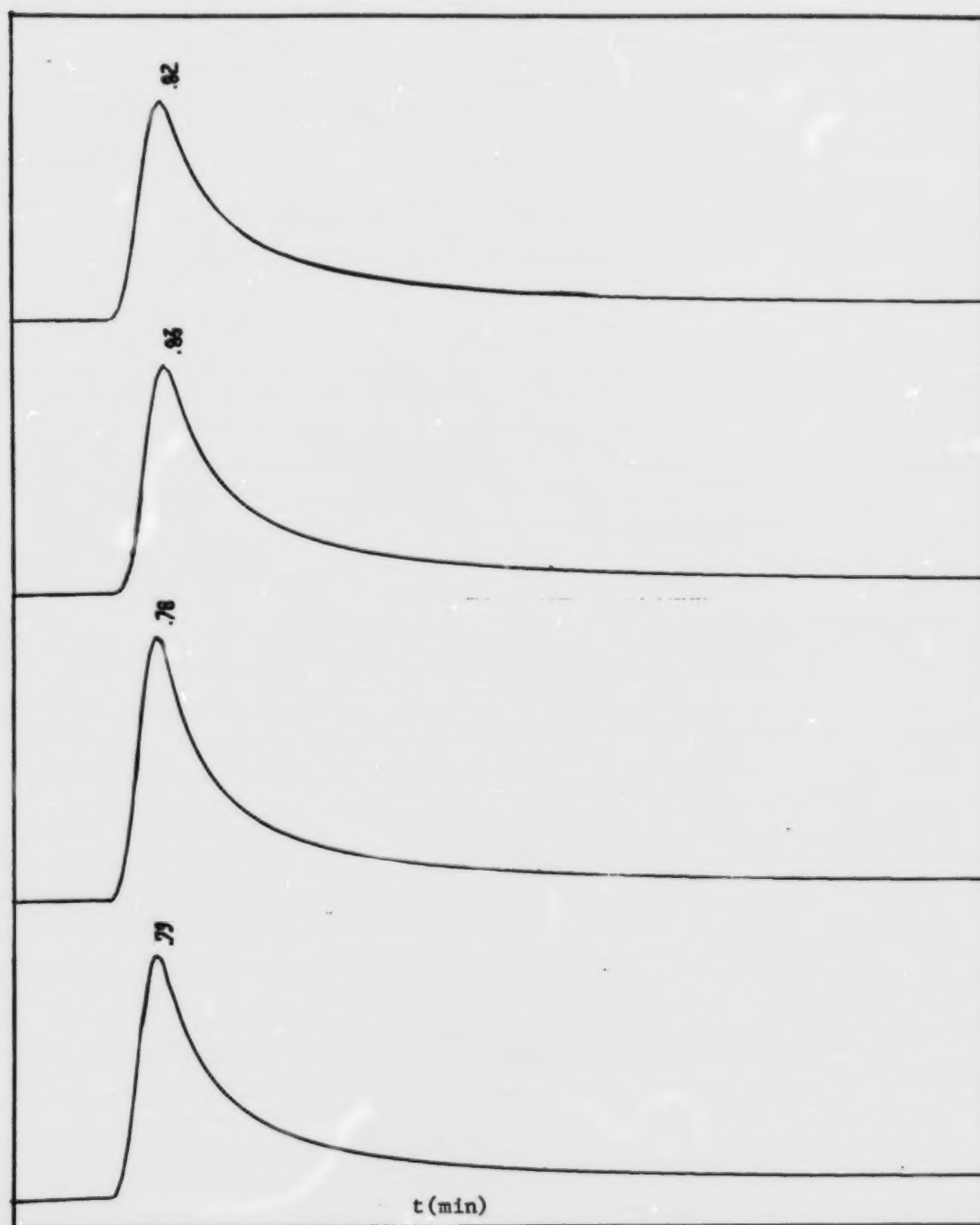


Figure III.20. Experimental chromatograms for the pyrrole/Na-mordenite system (30 cc/min; 100°C; 1 μL).

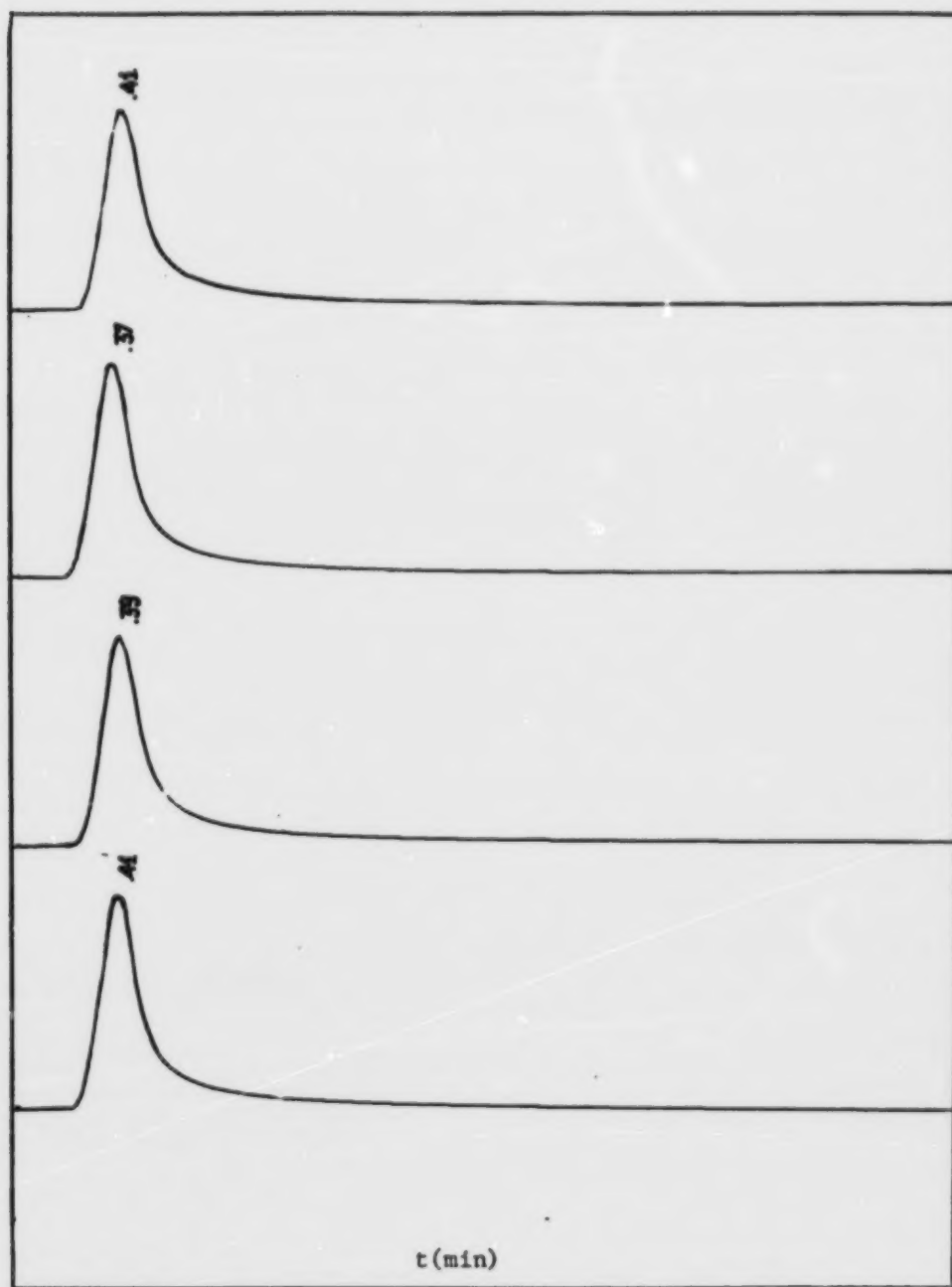


Figure III.21. Experimental chromatograms for the pyrrole/Na-mordenite system (30 cc/min; 125°C; 1 μL).

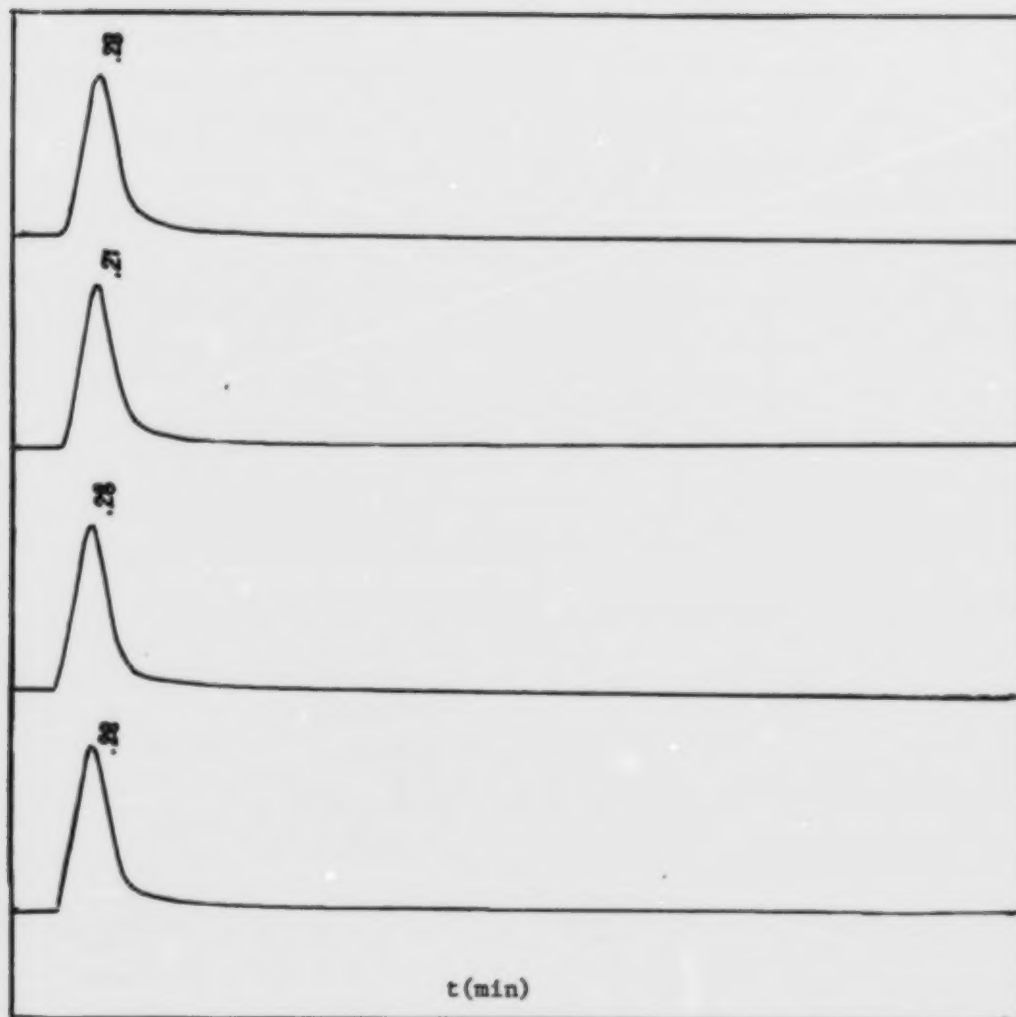


Figure III.22. Experimental chromatograms for the pyrrole/Na-mordenite system (30 cc/min; 150°C; 1 μL).

System: Pyrrole/Ca-mordenite (Fig. III.23 - III.25)

Bed parameters:

Weight of adsorbent : 1.28 g
 Packed bed length : 11.1 cm
 Particle size : 48/60 mesh

Table III.19 - Retention times of pyrrole in Ca-mordenite.

Inlet pulse (min)	Retention time (min)	Area: Input pulse (counts)	Area: Response signal (counts)
100°C, 30 cc/min			
(1 µL)			
0.13	0.36	1.90×10^6	1.79×10^6 (94%)
0.13	0.38	1.90×10^6	1.73×10^6 (91%)
0.13	0.37	1.90×10^6	1.78×10^6 (93%)
0.13	0.36	1.90×10^6	1.83×10^6 (96%)
0.13	0.36	1.90×10^6	1.81×10^6 (95%)
(0.5 µL)			
0.13	0.39	8.50×10^5	8.40×10^5 (99%)
0.13	0.40	8.50×10^5	8.53×10^5 (100%)
125°C, 30 cc/min			
(1 µL)			
0.12	0.27	1.91×10^6	1.86×10^6 (97%)
0.12	0.27	1.91×10^6	1.77×10^6 (92%)
0.12	0.25	1.91×10^6	1.73×10^6 (90%)
0.12	0.24	1.91×10^6	1.75×10^6 (92%)
0.12	0.25	1.91×10^6	1.75×10^6 (92%)
(0.5 µL)			
0.12	0.25	8.67×10^5	8.36×10^5 (96%)
0.12	0.25	8.67×10^5	8.43×10^5 (97%)
0.12	0.25	8.67×10^5	8.39×10^5 (96%)
0.12	0.25	8.67×10^5	8.40×10^5 (97%)
150°C, 30 cc/min			
(1 µL)			
0.12	0.21	1.90×10^6	1.75×10^6 (93%)
0.12	0.23	1.90×10^6	1.72×10^6 (92%)
(0.5 µL)			
0.12	0.20	8.67×10^5	8.23×10^5 (95%)
0.12	0.20	8.67×10^5	8.33×10^5 (96%)
0.12	0.20	8.67×10^5	8.31×10^5 (96%)

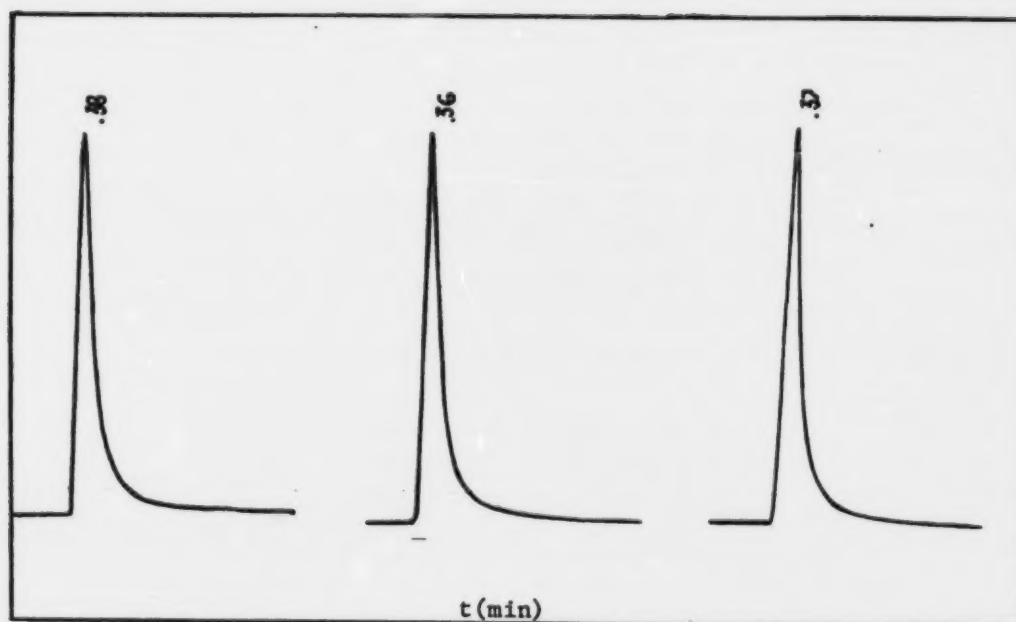


Figure III.23. Experimental chromatograms for the pyrrole/Ca-mordenite system (30 cc/min; 100°C; 1 μ L (0.5 μ L)).

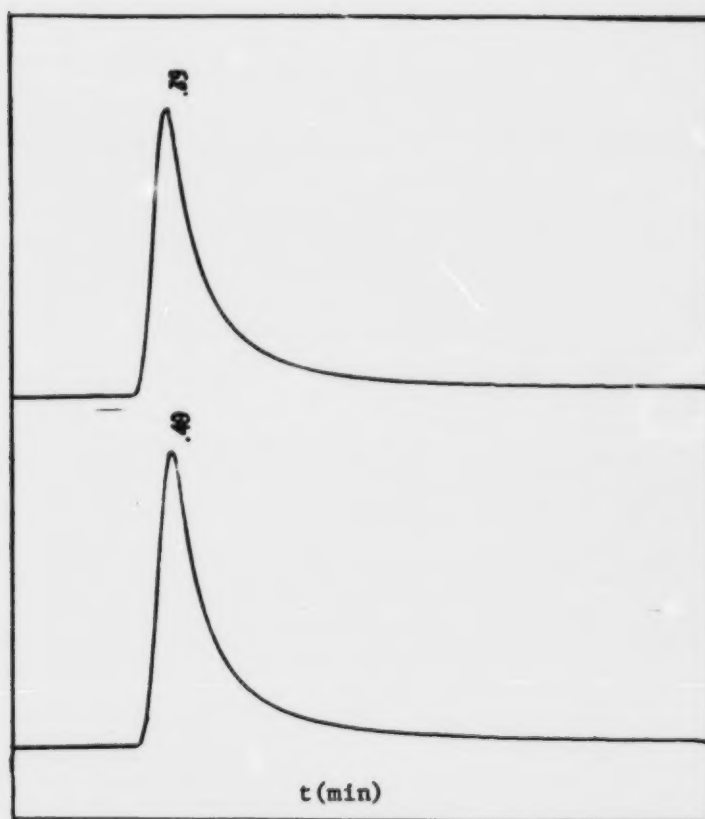


Figure III.23. (Continued)

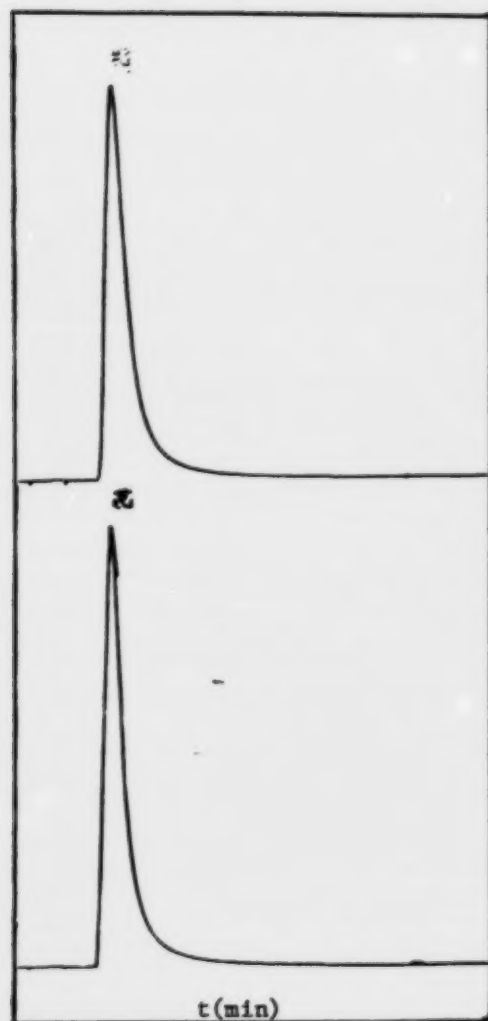


Figure III.24. Experimental chromatograms for the pyrrole/Ca-mordenite system (30 cc/min; 125°C; 1 μL (0.5 μL)).

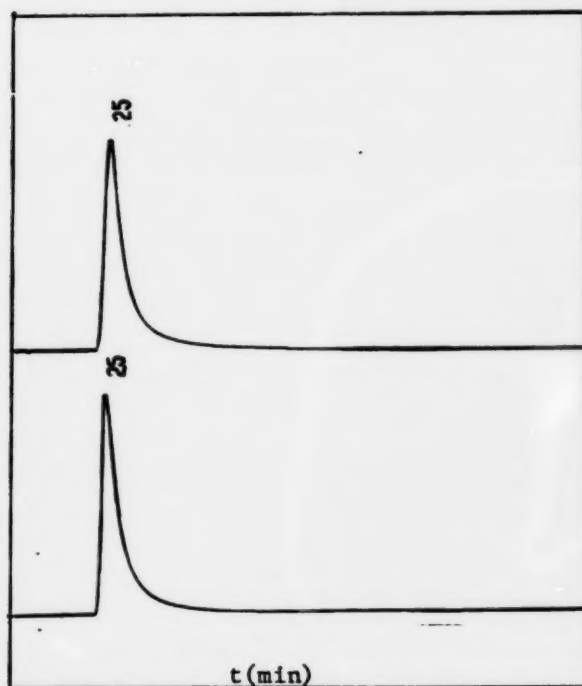


Figure III.24. (Continued)

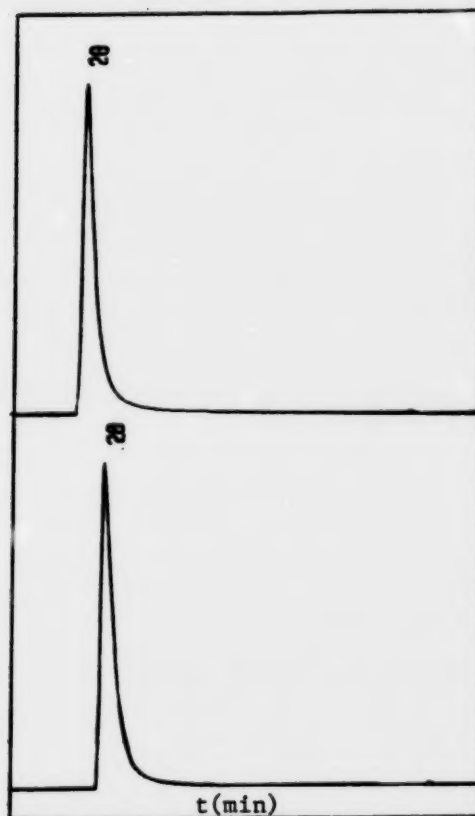


Figure III.25. Experimental chromatograms for the pyrrole/Ca-mordenite system (30 cc/min; 150°C; 1 μL (0.5 μL)).

conditions used they do not deviate from linearity significantly. This can be seen from the negligible effect of the injection volume on the response signal for the pyrrole/Ca-mordenite system (see table III.11 and figs. III.23 - III.25). Thus for these systems the linear chromatography theory may be used to describe the obtained experimental data.

III.2.8 Pyrrole/Na-ZSM5 system (Fig. II.26)

Bed parameters:

Weight of adsorbent: 1.05 g
 Packed bed length: 10.6 cm
 Particle size: 48/60

The results obtained with this system are given in figure III.26. The behaviour of the system is nonlinear and mirrors the behaviour of the pyridine/H-ZSM5 system. The response signals are highly dispersed and reasonable response signals are obtained only at higher temperatures and with large injection volumes. As was the case with pyridine/H-mordenite system, the response signals obtained with pyrrole/Na-mordenite system also exhibit very broad two distinct elution peaks (fig. III.26B, C, D).

III.2.9 Pyrrole/H-X; Pyrrole/Na-X and Pyrrole/Ca-X systems (Fig. III.27- Fig. III.29)

<u>Bed parameter:</u>	H-X	Na-X	Ca-X
Weight of adsorbent:	1.5	3.05	3.26 (g)
Packed bed length:	14.2	33.0	32.9 (cm)
Particle size	48/60	48/60	48/60 (mesh)

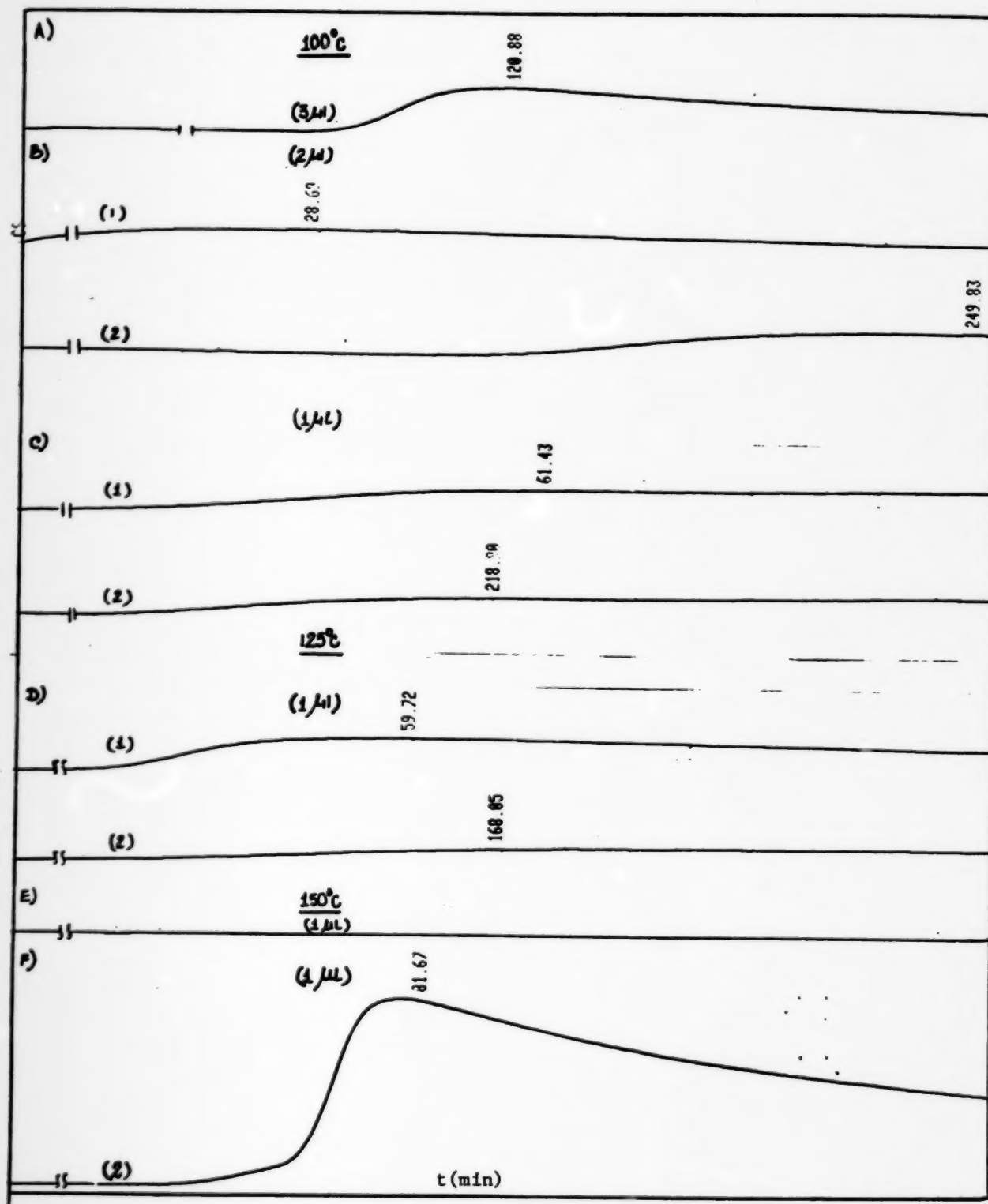


Figure III.26. Experimental chromatograms for the pyrrole/Na-ZSM5 system (30 cc/min).

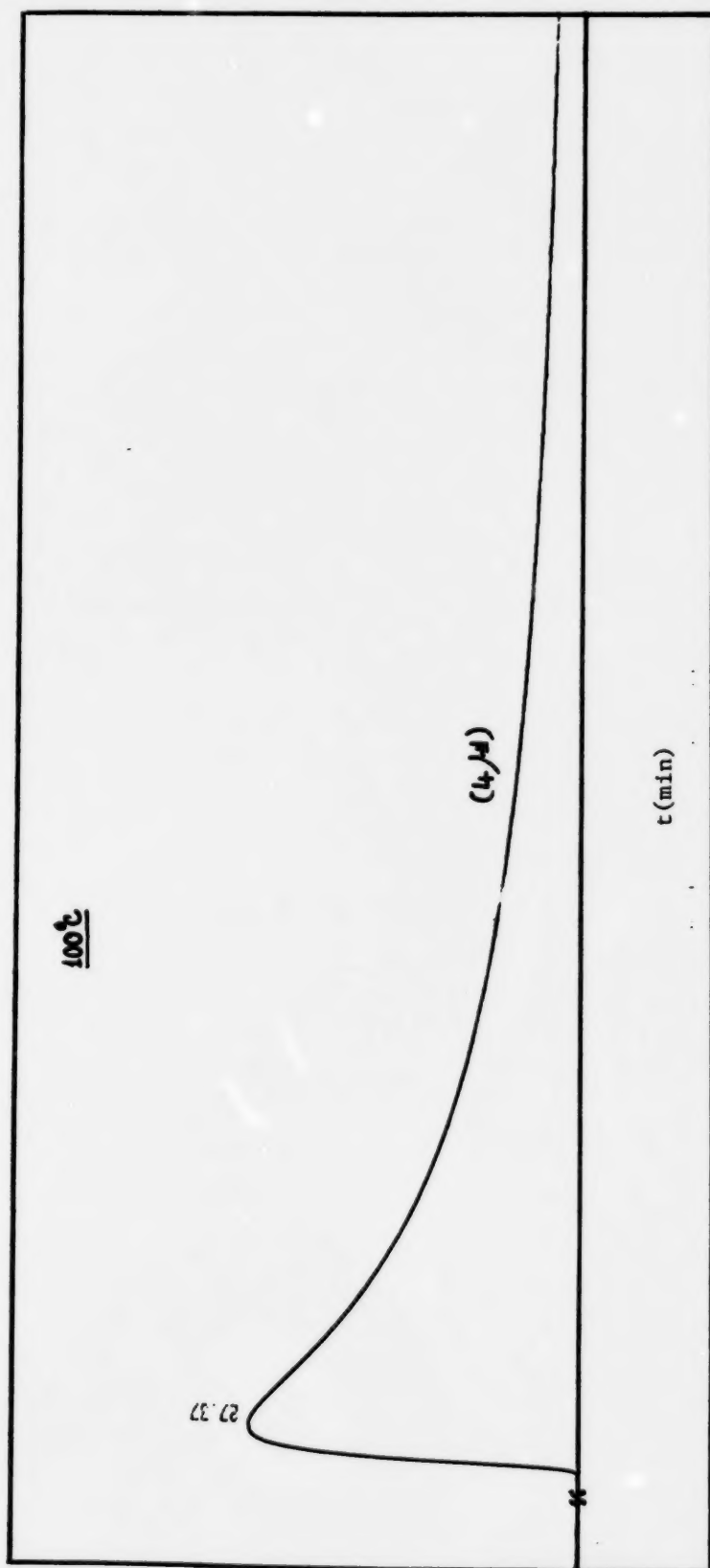


Figure III.27. Experimental chromatograms for the pyrrole/H-X system (30 cc/min; 100°C).

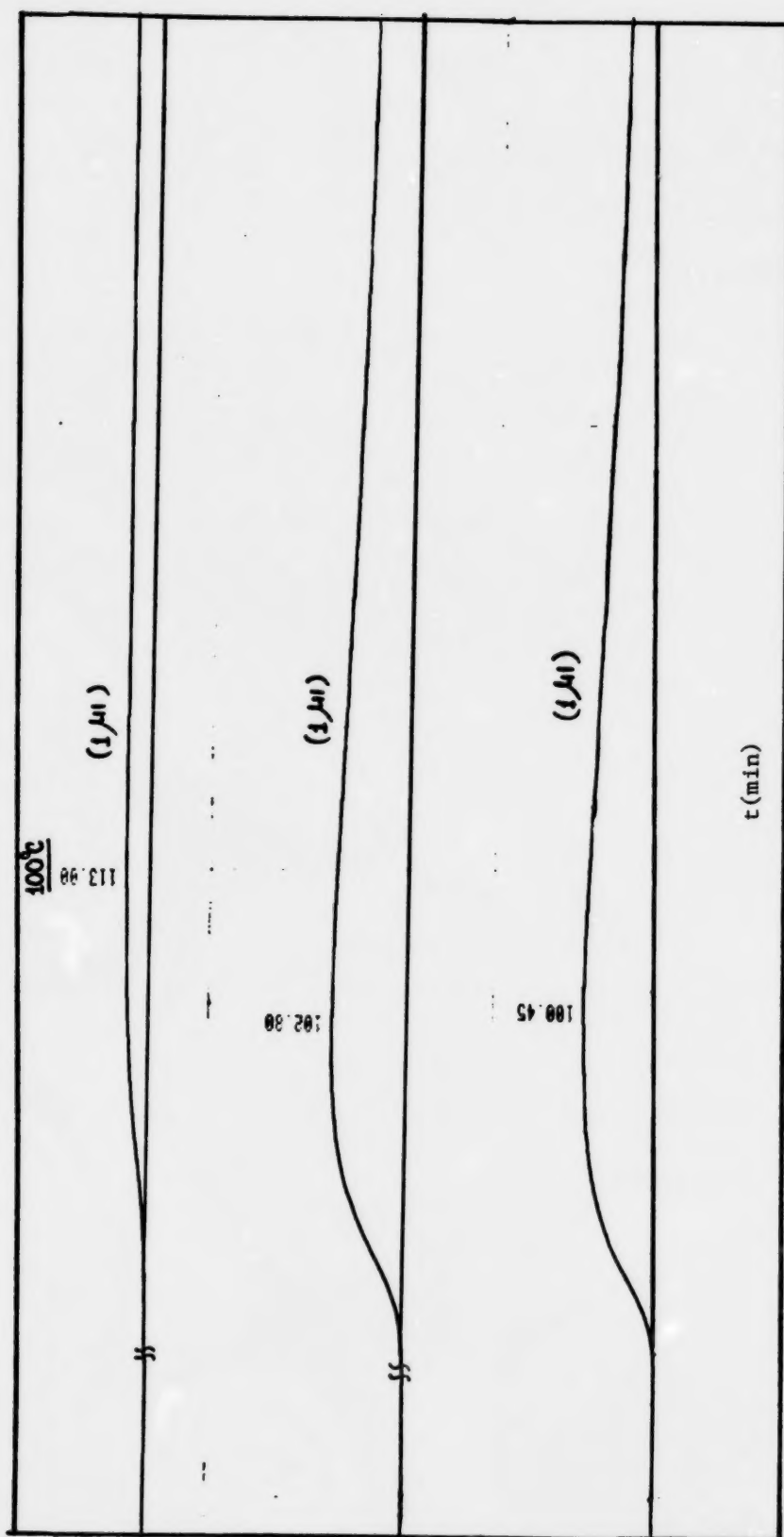


Figure III.27. (Continued)

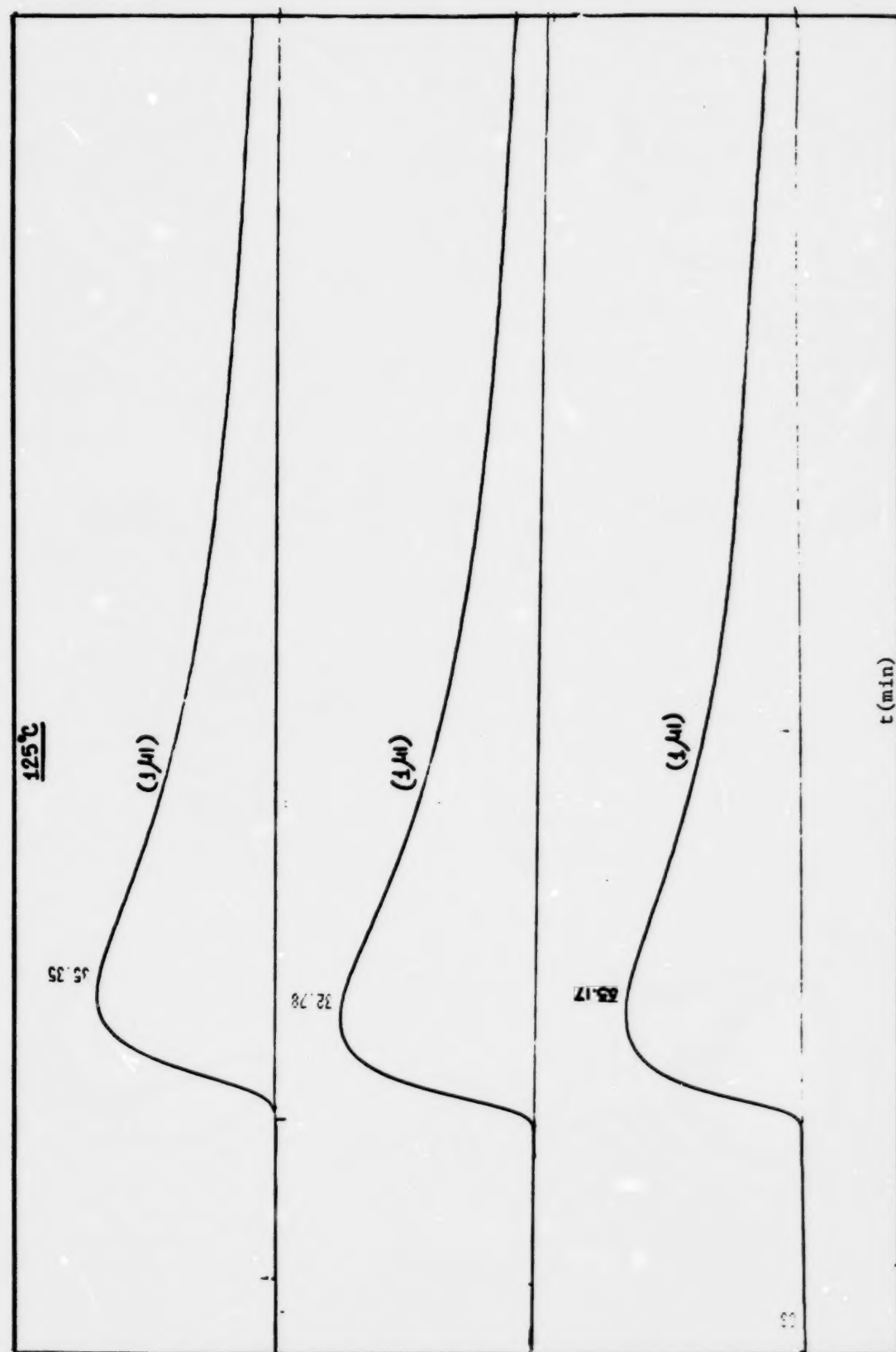


Figure III.28. Experimental chromatograms for the pyrrole/H-X system (30 cc/min; 125°C).

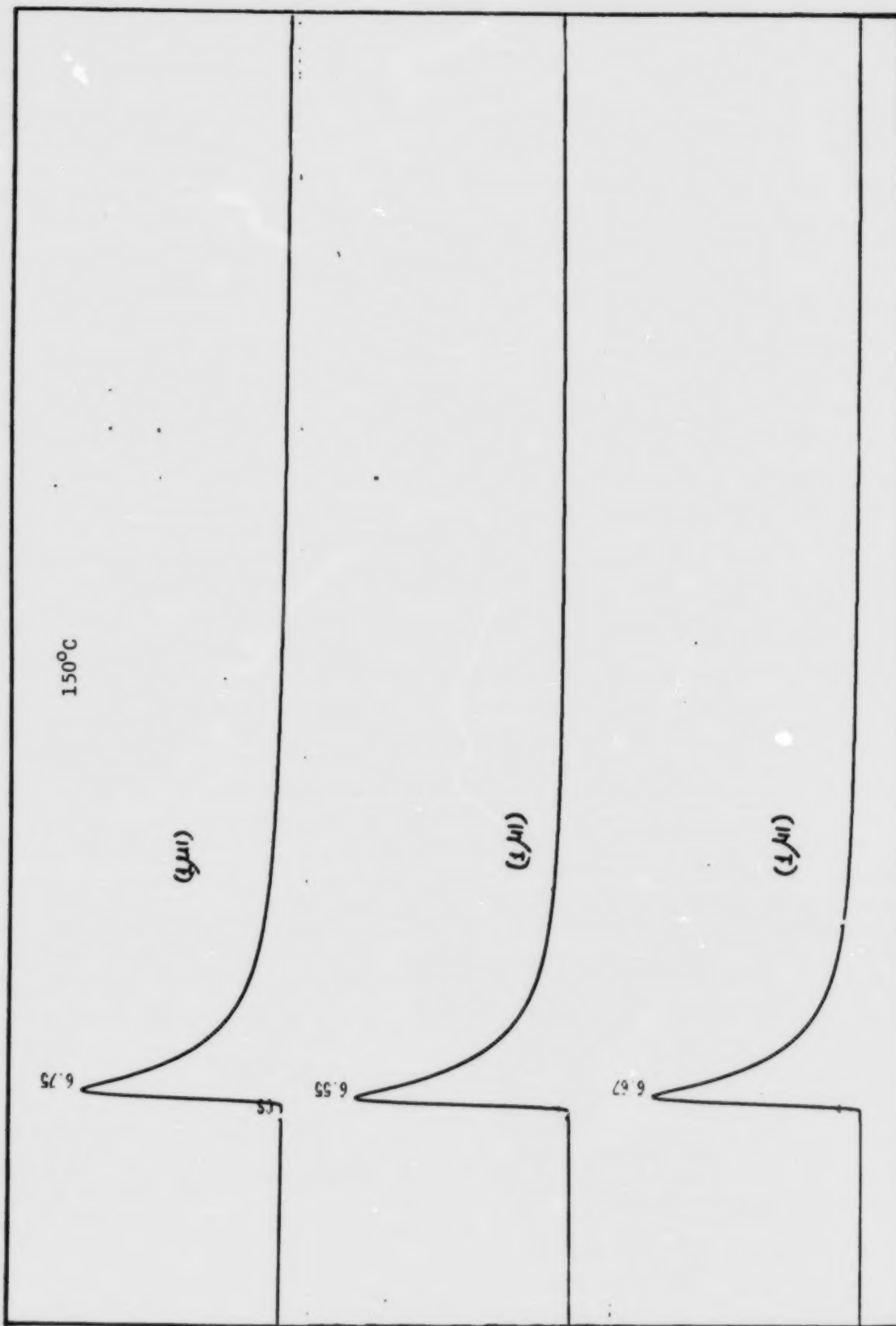


Figure III.29. Experimental chromatograms for the pyrrole/H-X system (30 cc/min; 150°C).

The experimental data obtained with these systems are reported in figures III.27 - III.29. Reasonable response signals are obtained only with the pyrrole/H-X system. With Na-X and Ca-X the obtained response signals are highly dispersed and appear as bumps in the baseline. Usually the elution times obtained are in the range of 10-12 hr even with large injection volumes ($\sim 5 \mu\text{L}$). With H-X the elution times obtained are significantly lower than for Na-X and Ca-X. The degree of dispersity of the response signals is greatest at low temperature. At high temperature ($\sim 150^\circ\text{C}$) the pyrrole pulse elutes with a sharp front followed by a finite tail. The behaviour of the pyrrole/H-X system parallels the behaviour of the pyrrole/Na-ZSM5 and other pyridine/zeolite systems investigated.

III.3 CORRECTIONS FOR THE AXIAL DISPERSION

Generally axial dispersion cannot be avoided in measurements of effective diffusivities by the gas chromatography technique. Usually the axial dispersion is measured with blank runs using nonporous particles similar in size and shape to the sample adsorbent. In this study a method very similar to the one proposed by Hsu and Haynes [27] is used. Small molecules such as N_2 ($3.0 \text{ \AA}$) and Ar ($3.84 \text{ \AA}$) were used to estimate the axial dispersion term from pulse dispersion measurements on the same packed bed of the zeolite adsorbent that is to be subjected to the pyridine and pyrrole pulses. The axial dispersion parameters may be obtained using the moment analysis of the pulse response data as described by Boniface and Ruthven [28]. Axial dispersion values also may be obtained using the van Deemter's equation [eq. (III.1)] or the dispersion equation [eq. (III.2)] as given in references [1,28].

$$\text{HETP} = a + \frac{b}{u} + cu \quad (3.1)$$

$$\frac{\text{HETP}}{u} = \frac{b}{u^2} + c \quad (3.2)$$

where: HETP : height equivalent to a theoretical plate

u : carrier gas velocity.

Through moment equations the coefficients b and c can be related to the system parameters. In the case of the van Deemter's equation a plot of HETP vs. u tends towards a straight line with slope c and at low velocities the curve tends towards a hyperbola which has an inverse slope b. A plot of the dispersion equation (HETP/u) vs. $1/u^2$ gives a straight line of slope b and intercept c. Since these coefficients (b, c) are related to the system parameters (50) axial dispersion coefficient may be evaluated from the plots using the van Deemter's equation [eq. (III.1)] or the dispersion equation [eq. (III.2)]. Axial dispersion data also may be evaluated using purely empirical correlations. Such an equation is given by Langer et al. [29].

$$D_{ax} = T_a D_m + \frac{P R_m u}{1 + (B D_m / R_m u)} \quad (3.3)$$

where: D_{ax} : axial dispersion

D_m : molecular diffusivity

u : interstitial velocity

T_a , P, B are semi-empirical constants which depend on the particle size and bed voidage.

From dimensional analysis it has been shown that for gases the particle Peclet number (Pe) can be correlated with the product of the particle Reynolds number (Re) and the Schmidt number (Sc) [27]. Hsu and Haynes [27]

have shown that when Pe is plotted against the product $Re \times Sc$ for a number of species differing in molecular size they fall on a common line. Thus axial dispersion coefficients for other molecules may be calculated from such correlations obtained with simpler molecules such as N_2 and Ar for the same bed.

N_2 pulse response data may also be used to evaluate the effect of the exchanged cations and the effect of the pyridine and pyrrole saturation of the adsorbents on the effective diffusivities. For this reason N_2 pulse response data were also obtained with zeolite packed beds before and after saturating the bed with pyridine and pyrrole. Such data are reported herein.

III.4 N_2 /ZEOLITE SYSTEMS

The system linearity tests for N_2 /zeolite systems are reported in table III.20 and figure III.30 for three different cationic forms of morde-nite.

As can be seen in figures III.30 - III.32 and table III.20, the injection volume of N_2 has a slight effect on the retention times and the response signals are assymmetric with large injection volumes (> 0.5 mL). At low injection volumes (< 0.2 mL) the response signal becomes symmetric (gaussian), and the retention times are insensitive to variations in the injection volume. This is an indication to the system linearity in this region and the linear chromatography theory can be applied to describe the chromatographic data.

System:	<u>N₂/H-mordenite</u> (Fig. III.30)	<u>N₂/Na-mordenite</u> (Fig. III.31)	<u>N₂/Ca-mordenite</u> (Fig. III.32)
Weight (absorbent):	1.5 g	1.45 g	1.28 g
Bed length:	12.5 cm	11.5 cm	11.1 cm
Particle size:	28/32 mesh	28/32 mesh	48/60 mesh
Flow rate:	15 cc/min	15 cc/min	15 cc/min
Temperature:	100°C	100°C	100°C

Table III.20 - Retention times of N₂ in zeolites.

Injection volume cc	Average retention time min	Injection volume cc	Average retention time min	Injection volume cc	Average retention time min
1.0	-	1.0	0.38	1.0	-
0.5	0.28	0.5	0.44	0.5	-
0.25	0.30	0.25	-	0.25	-
0.20	-	0.20	0.50	0.20	-
0.10	0.32	0.10	0.51	0.10	0.18
0.05	-	0.05	0.51	0.05	0.21
0.025	-	0.025	-	0.025	0.21

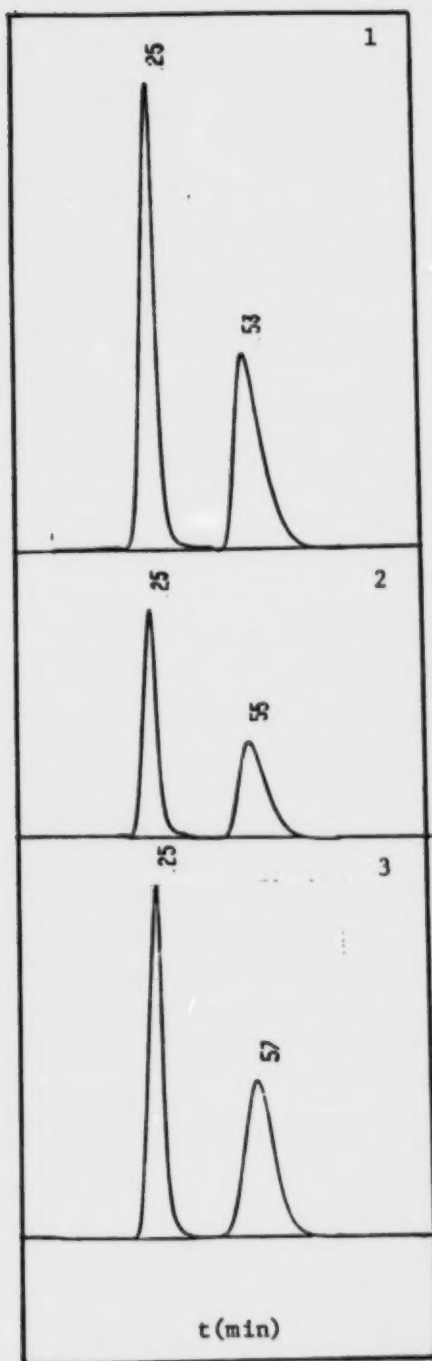


Figure III.30. Experimental chromatograms for the N_2/H -mordenite system (15 cc/min); 100°C).
1) 0.5 mL; 2) 0.25 mL; 3) 0.1 mL.

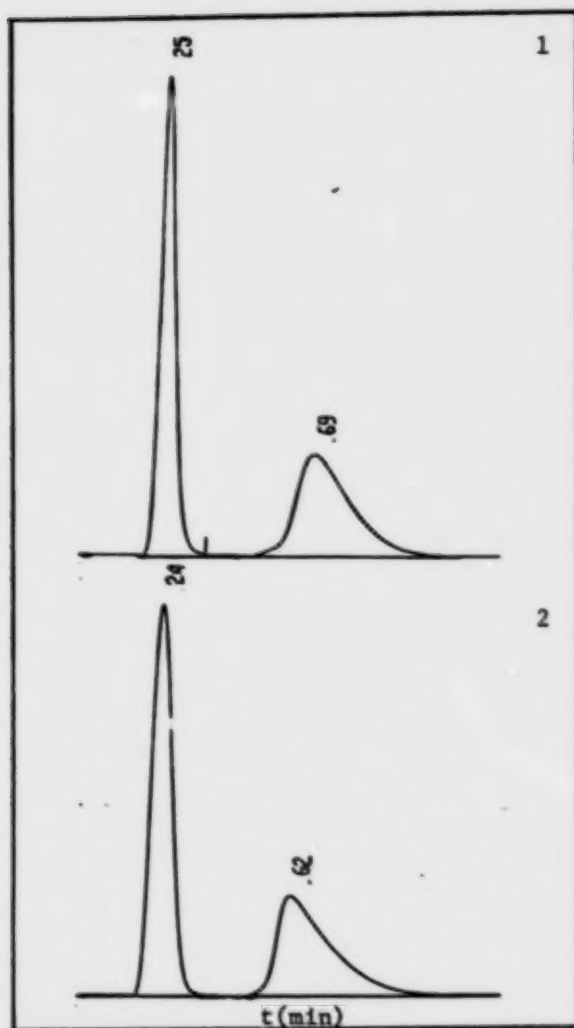


Figure III.31. Experimental chromatograms for the $\text{N}_2/\text{Na-mordenite}$ system (15 cc/min; 100°C).
1) 0.5 mL; 2) 1 mL; 3) 0.05 mL; 4) 0.1 mL; 5) 0.2 mL.

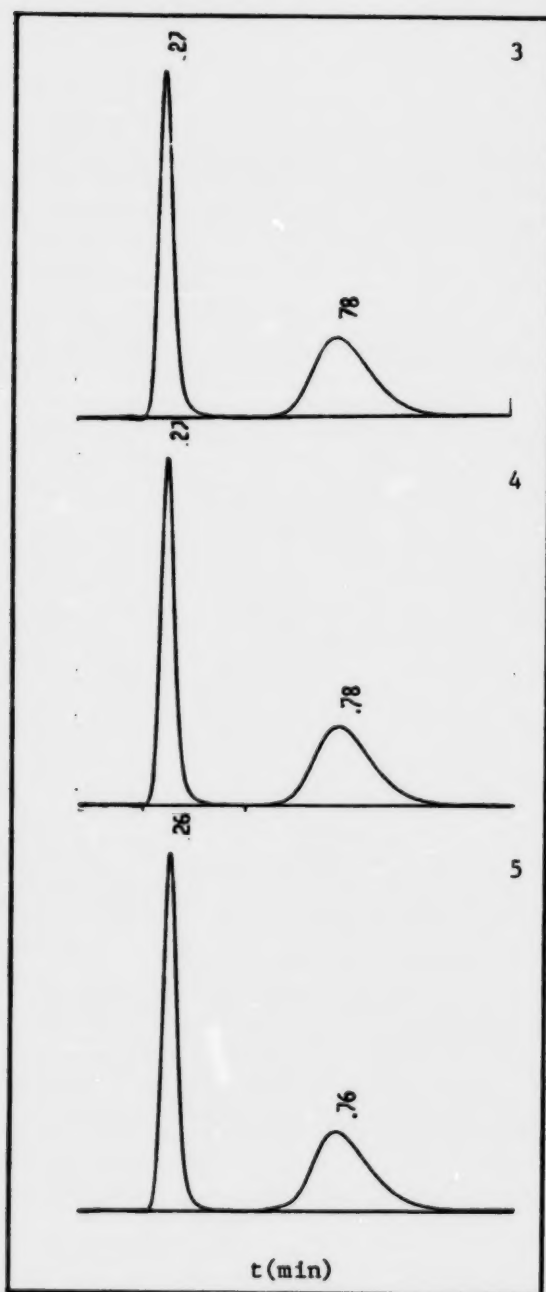


Figure III.31. (Continued)

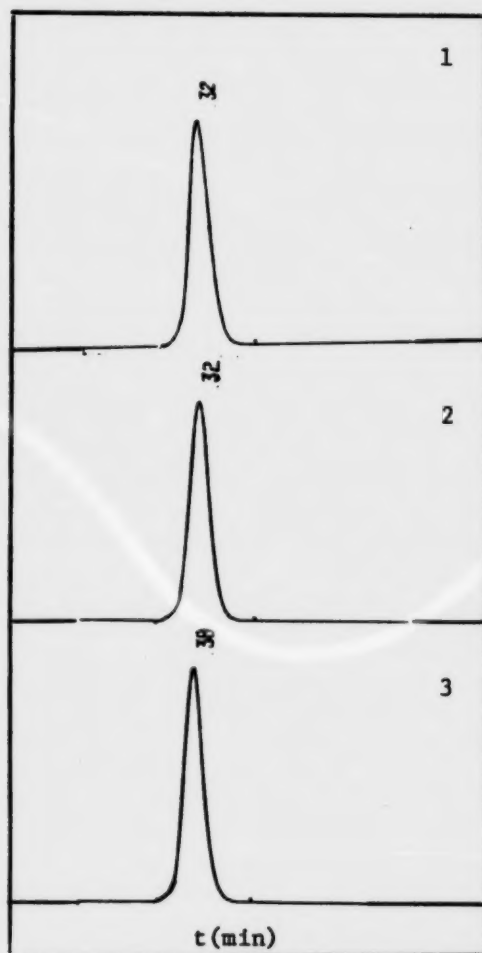


Figure III.32. Experimental chromatograms for the N_2 /Ca-mordenite system (30 cc/min; 100°C).
1) 0.025 mL; 2) 0.05 mL; 3) 0.1 mL.

III.5 THE EFFECT OF PYRIDINE (PYRROLE) ADSORPTION ON N₂ PULSE RESPONSE DATA

The effect of pyridine (pyrrole) saturation of the zeolite beds on the N₂ diffusivities was investigated by obtaining N₂ pulse response data with freshly packed zeolite beds and with the same beds after pyridine (pyrrole) saturation. At the same time these data may also be used to investigate the effect of various cations on N₂ diffusivities. These data were obtained only after a preliminary verification of the system linearity, in order that linear chromatography theory could be applied to describe the pulse response data. Some of these data are reported below for various N₂/zeolite systems.

Pulse response data for the N₂/H-mordenite system and the effect of the pyridine saturation of the bed on these data are reported in table III.21 and figures III.33 and III.34.

The retention times of N₂ are slightly lower for the pyridine saturated bed than for the fresh bed, under identical operation conditions. This may have resulted probably from a partial obstruction of the pores by the adsorbed pyridine. This aspect of pore blocking or obstruction by the adsorbed molecules was investigated in detail for several systems and these results are reported in tables III.22 - III.26 and figures III.35 - III.64 for some. For the N₂/H-mordenite system, the saturation of the bed by pyrrole had a significant effect on the N₂ retention times only at low temperature and flow rates (table III.22 and figs. III.35 - III.40).

Bed parameters:

Weight of adsorbent : 1.5 g
Bed length : 12.5 cm
Particle size : 28/32 mesh
Flow rate : 15 cc/min
Temperature : 100°C

Table III.21 - Effect of pyridine saturation on the N₂ retention times in H-mordenite. (Fig. III.33; Fig. III.34)

Volume injected cc	Average retention Time (min) (Fresh bed)	Average retention Time (min) (Pyridine saturated bed)
0.50	0.28	0.25
0.25	0.30	-
0.10	0.32	0.27
0.05	-	0.27

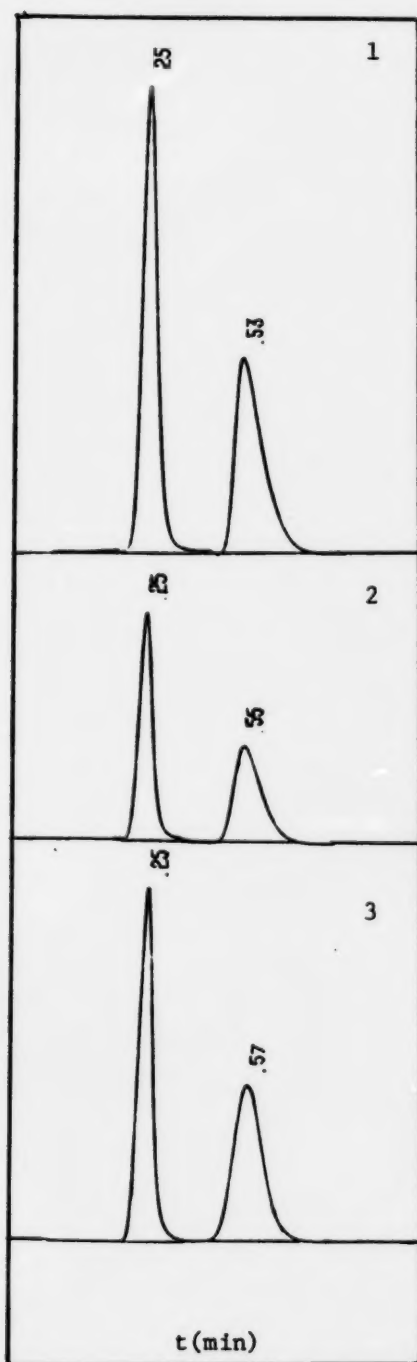


Figure III.33. Experimental chromatograms for the N_2/H -mordenite system (Fresh bed) (15 cc/min; 100°C).
1) 0.5 mL; 2) 0.25 mL; 3) 0.1 mL.

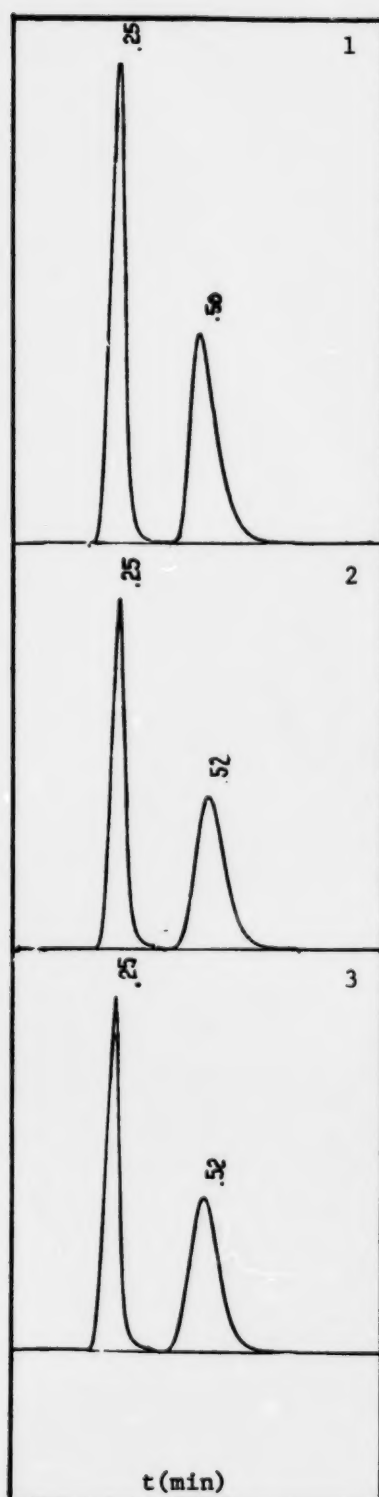


Figure III.34. Experimental chromatograms for the N /H-mordenite system (Pyridine saturated) (15 cc/min; 100°C).
1) 0.5 mL; 2) 0.1 mL; 3) 0.05 mL.

Bed parameters:

Weight of adsorbent : 3.89 g
 Bed length : 32.9 cm
 Particle size : 48/60 mesh
 Pulse size : 100 L

Table III.22 - Effect of pyrrole saturation on the N₂ retention times in H-mordenite. (Fig. III.35 - III.40)

Flow rate (cc/min)	Fresh bed			Pyrrole saturated bed		
	Temperature °C			Temperature °C		
	100	125	150	100	125	150
15	0.65	0.47	0.38	0.59	0.46	0.37
30	0.32	0.24	0.19	0.29	0.23	0.18
45	0.22	0.17	0.13	0.20	0.16	0.13

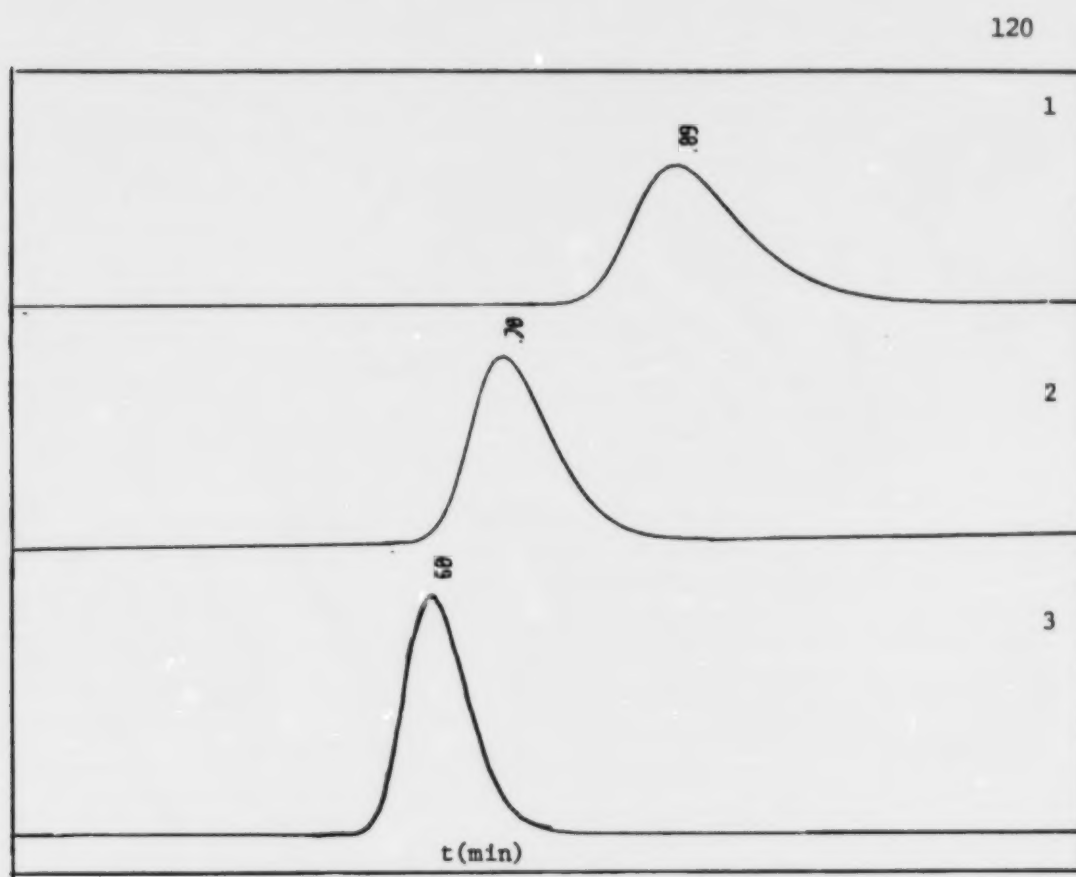


Figure III.35. Experimental chromatograms for the N_2/H -mordenite system (Fresh bed) (15 cc/min; 0.1 mL).
1) 100°C; 2) 125°C; 3) 150°C.

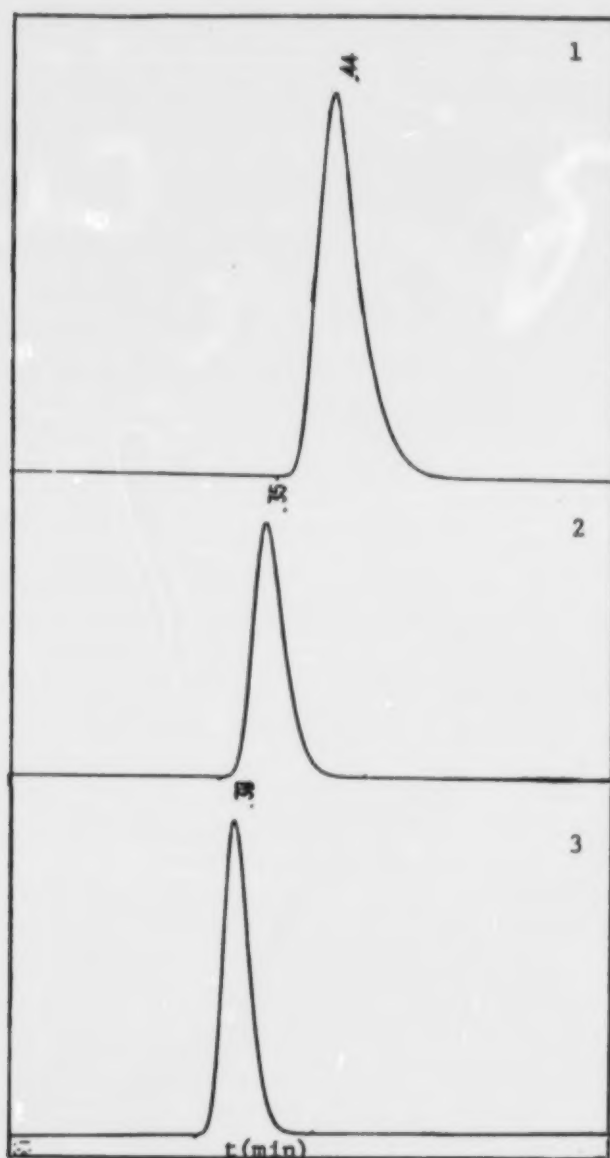


Figure III.36. Experimental chromatograms for the N_2/H -mordenite system (Fresh bed) (30 cc/min; 0.1 mL).
1) 100°C; 2) 125°C; 3) 150°C.

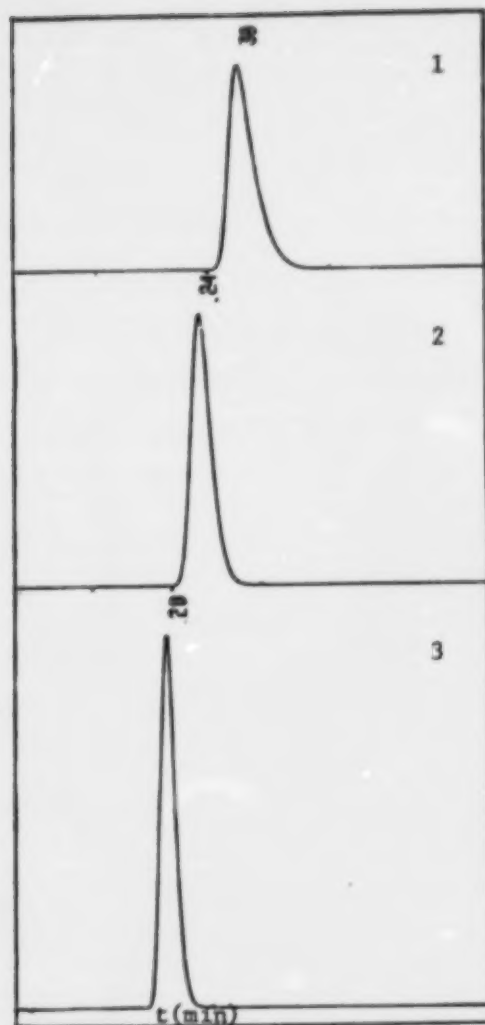


Figure III.37. Experimental chromatograms for the N_2/H -mordenite system (Fresh bed) (45 cc/min; 0.1 mL).
1) 100°C; 2) 125°C; 3) 150°C.

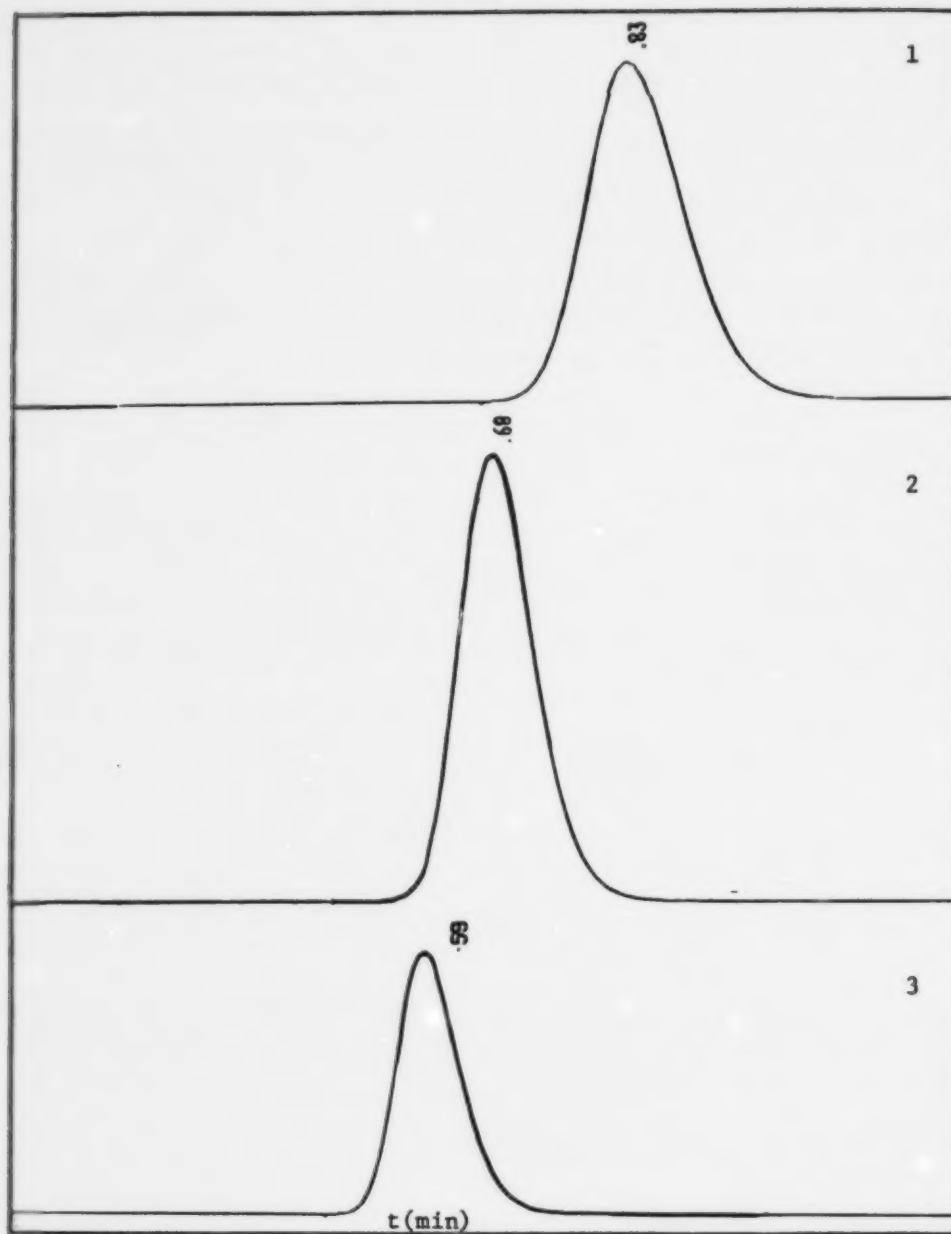


Figure III.38. Experimental chromatograms for the N_2/H -mordenite system (Pyridine saturated) (15 cc/min; 0.1 mL).
1) 100°C; 2) 125°C; 3) 150°C.

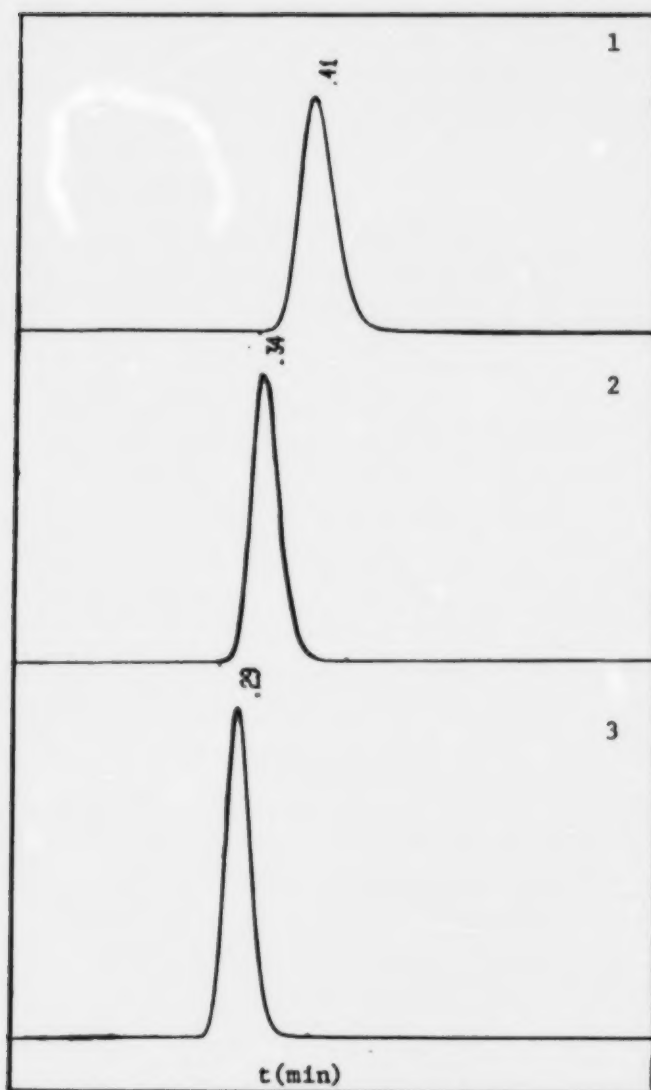


Figure III.39. Experimental chromatograms for the N_2/H -mordenite system (Pyridine saturated) (30 cc/min; 0.1 mL).
1) 100°C; 2) 125°C; 3) 150°C.

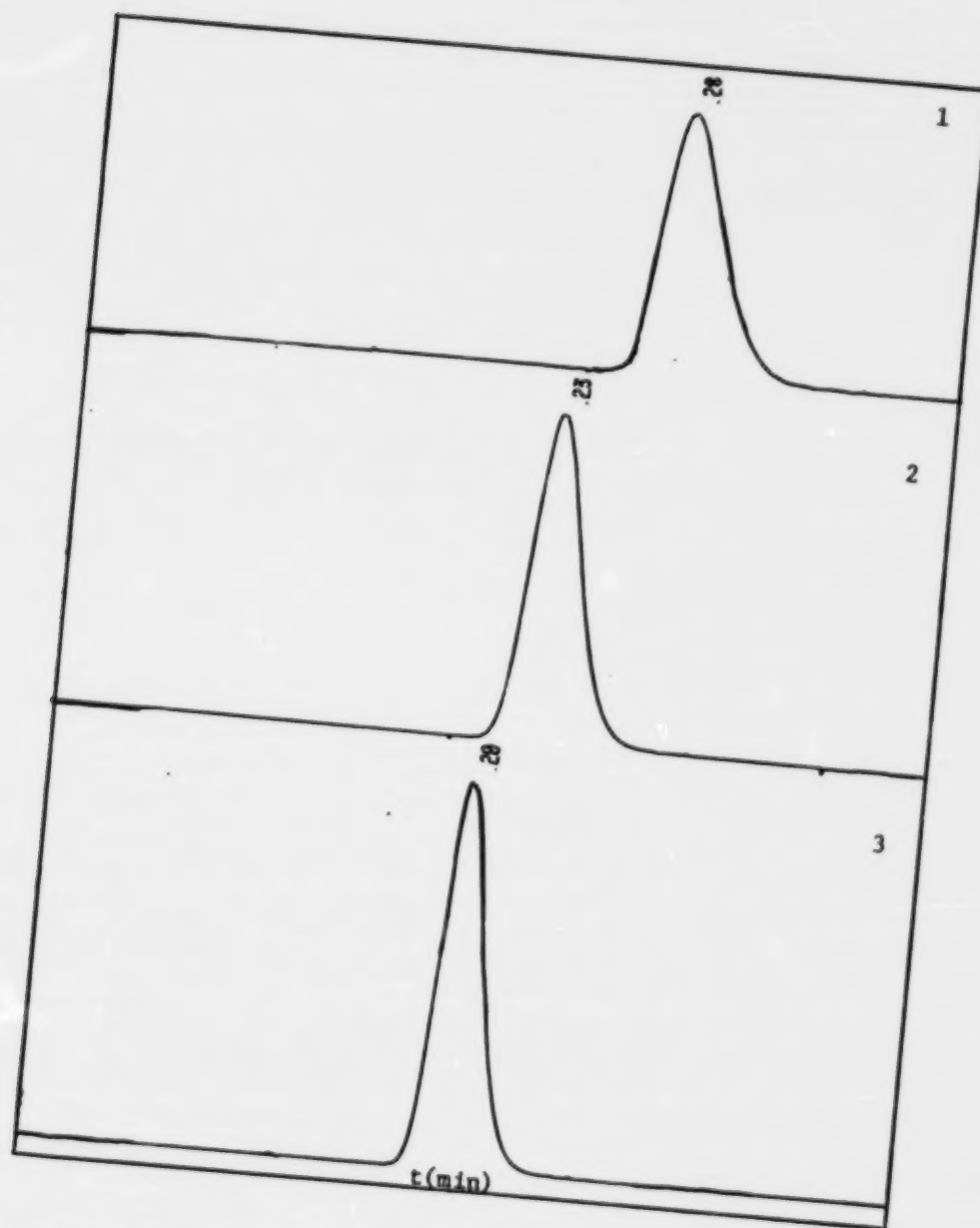


Figure III.40. Experimental chromatograms for the N_2/H -mordenite system (Pyridine saturated) (45 cc/min; 0.1 mL).
1) 100°C; 2) 125°C; 3) 150°C.

Bed parameters:

Weight of adsorbent : 3.5 g
 Bed length : 32.9 cm
 Particle size : 48/60 mesh
 Pulse size : 100 L

Table III.23 - Effect of pyridine saturation on the N₂ retention times in H-ZSM5. (Fig. III.41 - III.46)

Flow rate (cc/min)	Fresh bed			Pyridine saturated bed		
	Temperature °C			Temperature °C		
	100	125	150	100	125	150
15	0.66	0.51	0.43	0.51	0.42	0.36
30	0.35	0.28	0.23	0.27	0.23	0.19
45	0.25	0.20	0.16	0.19	0.17	0.14

Bed parameters:

Weight adsorbent : 3.05 g
 Bed length : 33.0 cm
 Particle size : 48/60 mesh
 Pulse size : 100 L

Table III.24 - Effect of pyrrole saturation on the N₂ retention times in Na-x. (Fig. III.47 - III.52)

Flow rate (cc/min)	Fresh bed			Pyrrole saturated bed		
	Temperature °C			Temperature °C		
	100	125	150	100	125	150
15	0.63	0.50	0.42	0.27	0.25	0.26
20	0.32	0.26	0.21	0.14	0.13	0.14
45	0.22	0.19	0.15	0.10	0.10	0.09

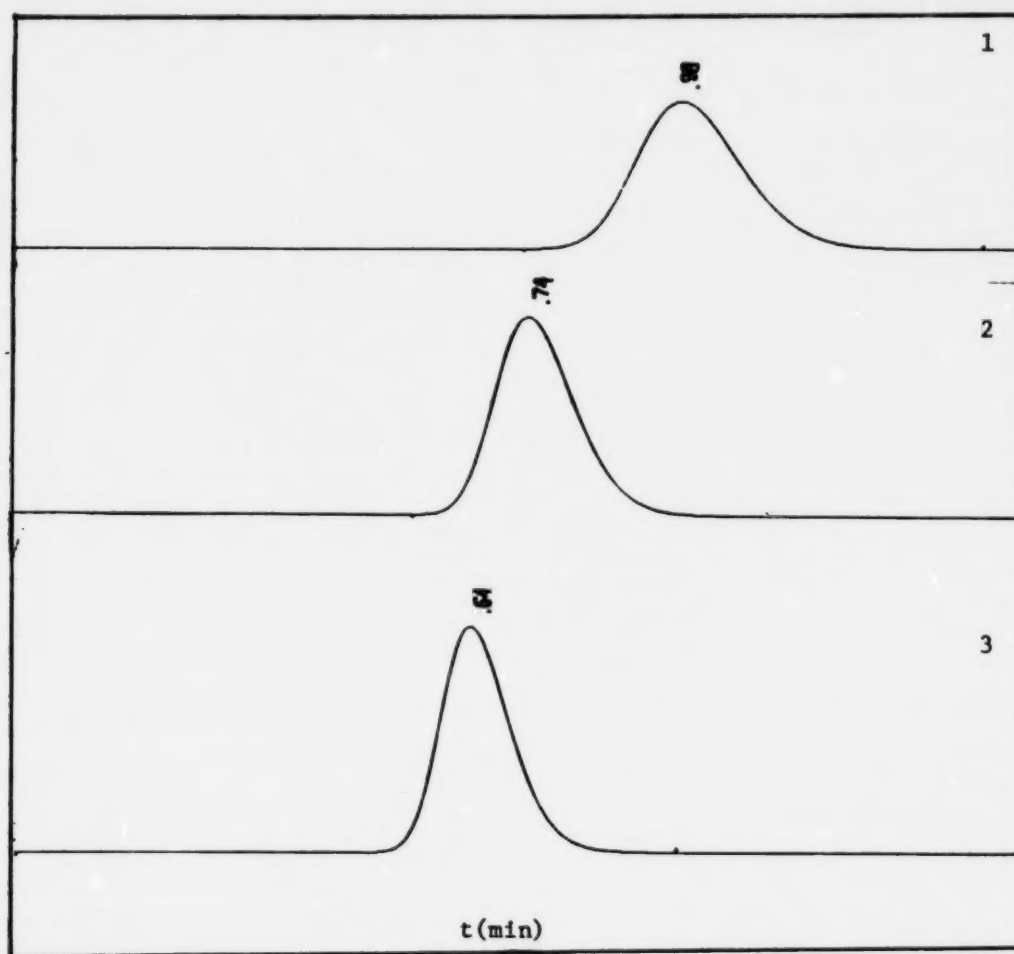


Figure III.41. Experimental chromatograms for the N_2/H -ZSM5 system (Fresh bed) (15 cc/min; 0.1 mL).
1) 100°C; 2) 125°C; 3) 150°C.

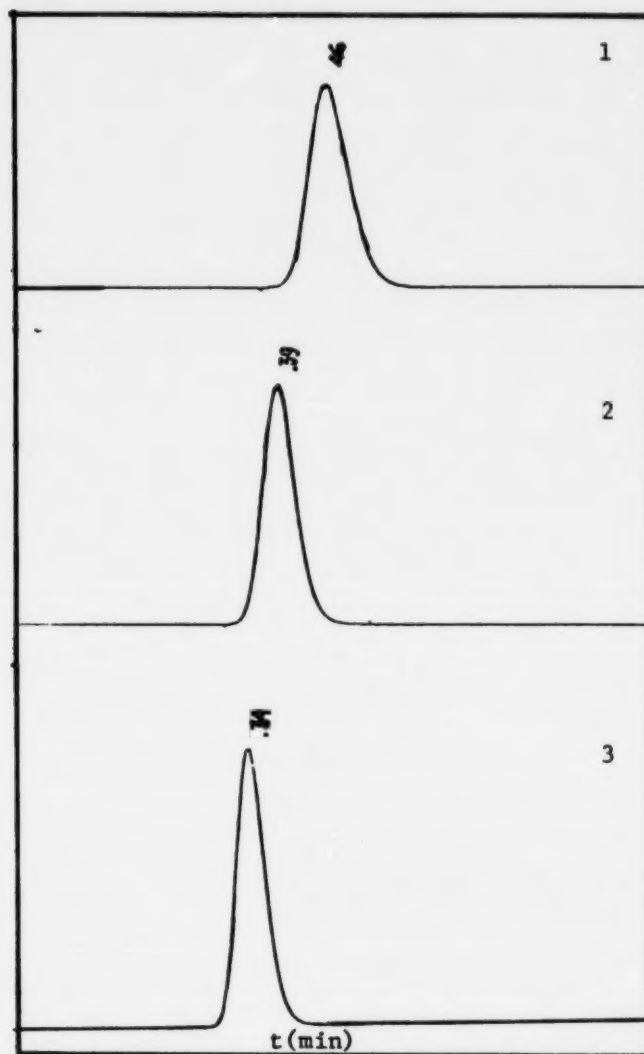


Figure III.42. Experimental chromatograms for the N_2/H -ZSM5 system (Fresh bed) (30 cc/min; 0.1 mL).
1) 100°C; 2) 125°C; 3) 150°C.

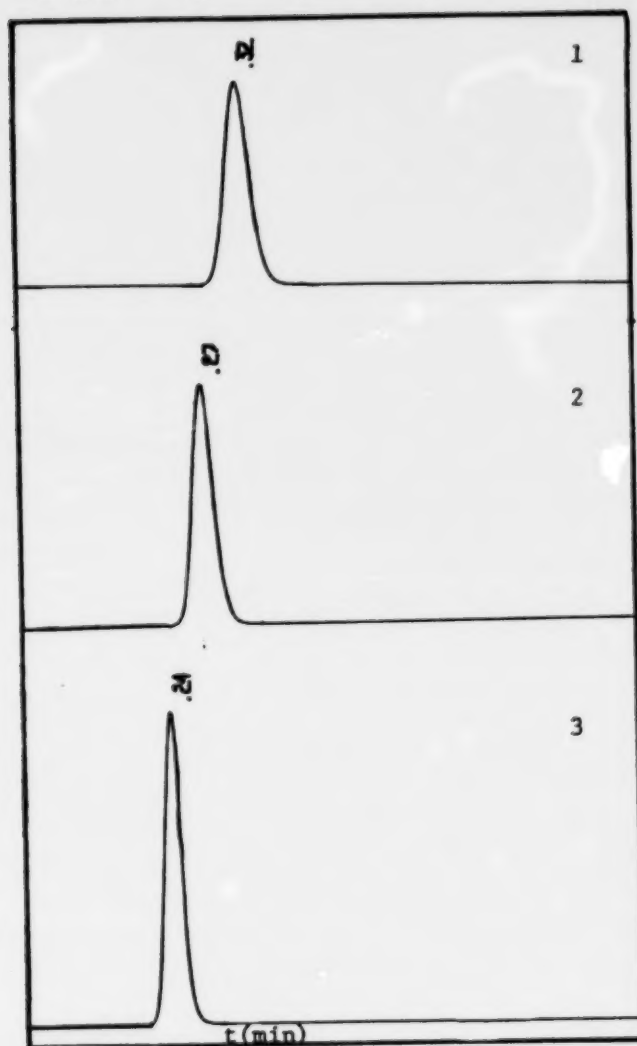


Figure III.43. Experimental chromatograms for the N_2/H -ZSM5 system (Fresh bed) (45 cc/min; 0.1 mL).
1) 100°C; 2) 125°C; 3) 150°C.

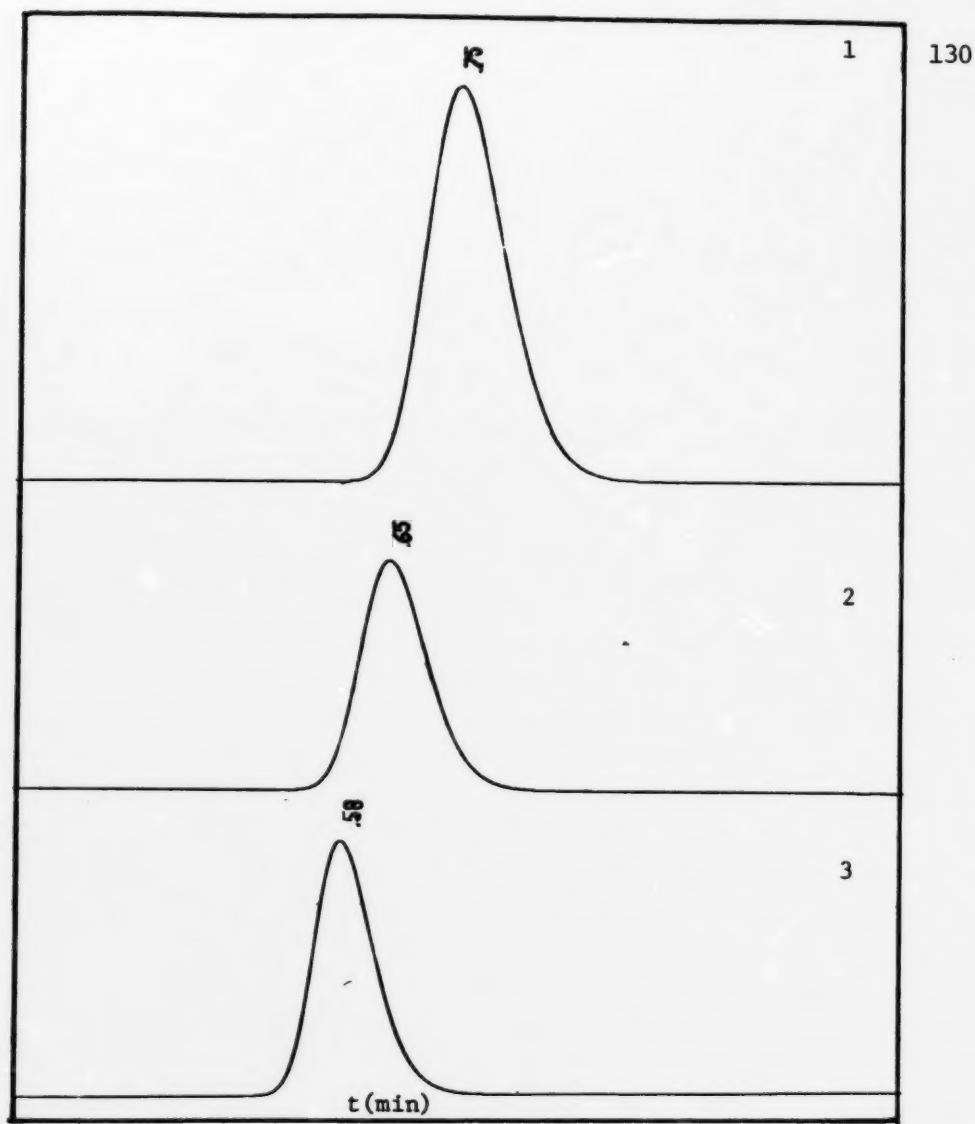


Figure III.44. Experimental chromatograms for the N_2/H -ZSM5 system (Pyridine saturated) (15 cc/min; 0.1 mL).
1) 100°C; 2) 125°C; 3) 150°C.

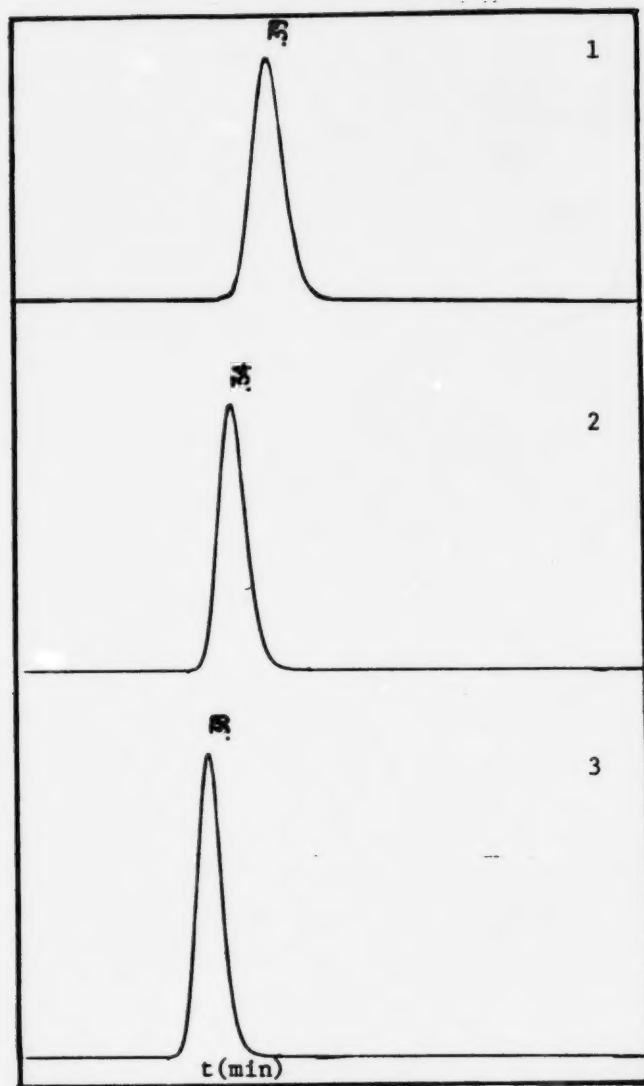


Figure III.45. Experimental chromatograms for the N_2/H -ZSM5 system (Pyridine saturated) (30 cc/min; 0.1 mL).
1) 100°C; 2) 125°C; 3) 150°C.

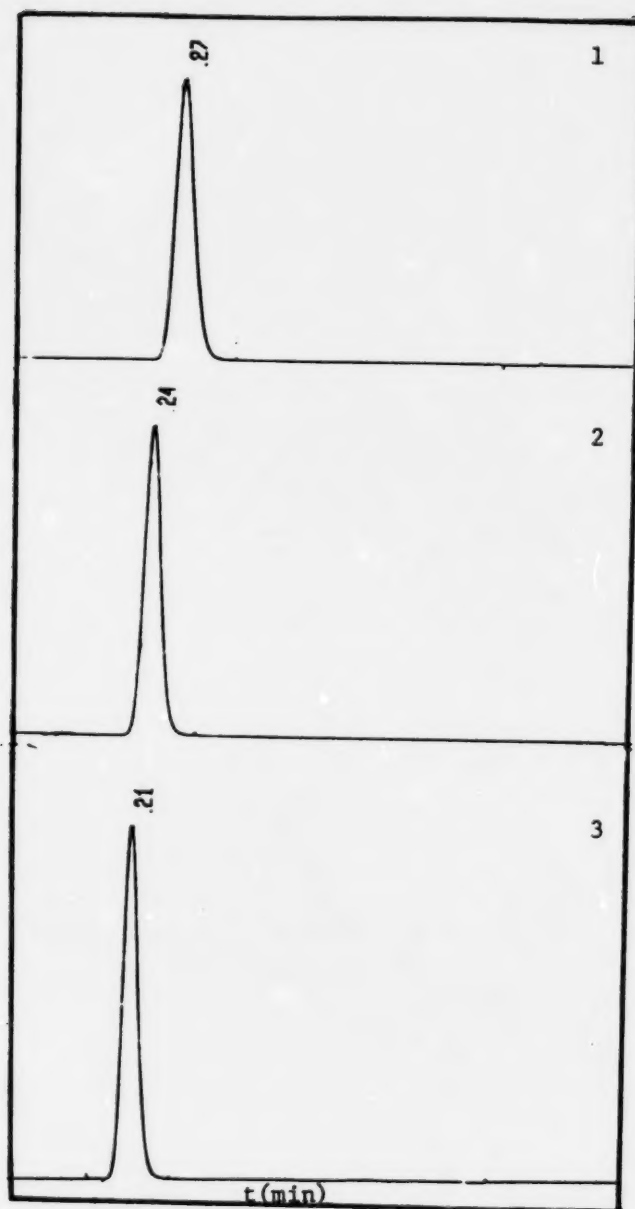


Figure III.46. Experimental chromatograms for the N_2/H -ZSM5 system (Pyridine saturated) (45 cc/min; 0.1 mL).
1) 100°C; 2) 125°C; 3) 150°C.

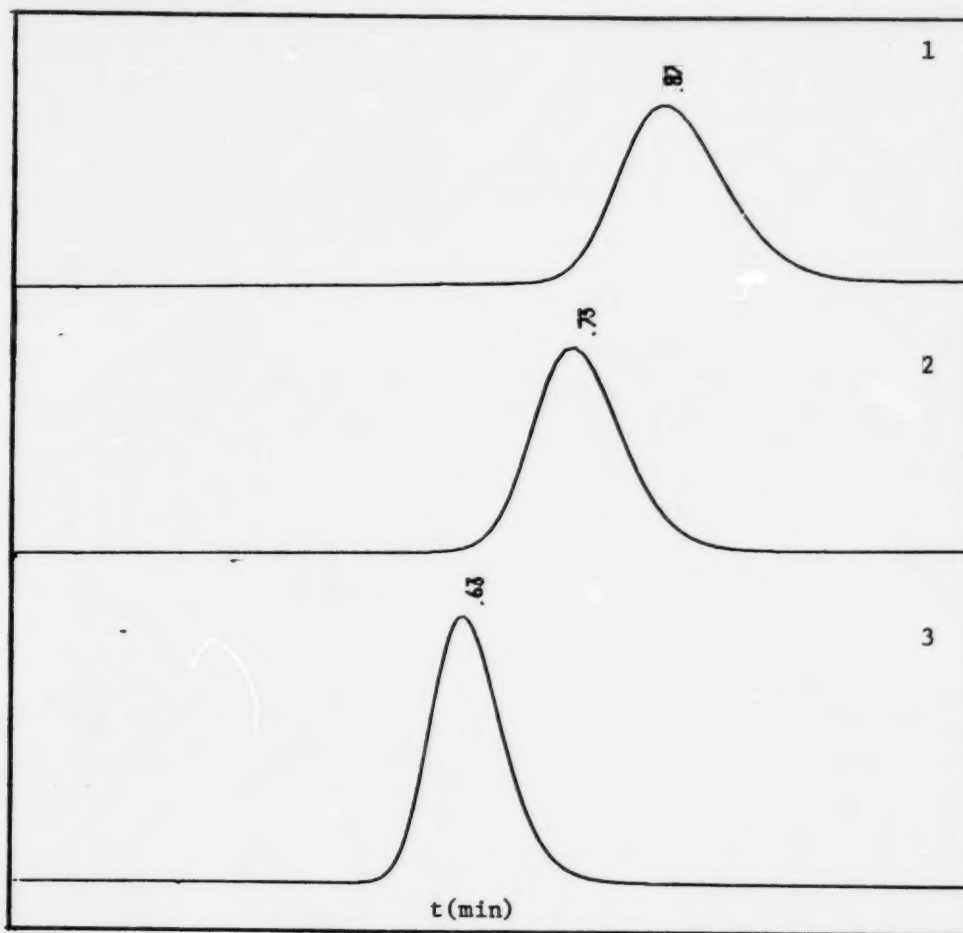


Figure III.47. Experimental chromatograms for the $N_2/Na-X$ system (Fresh bed) (15 cc/min; 0.1 mL).
1) 100°C; 2) 125°C; 3) 150°C.

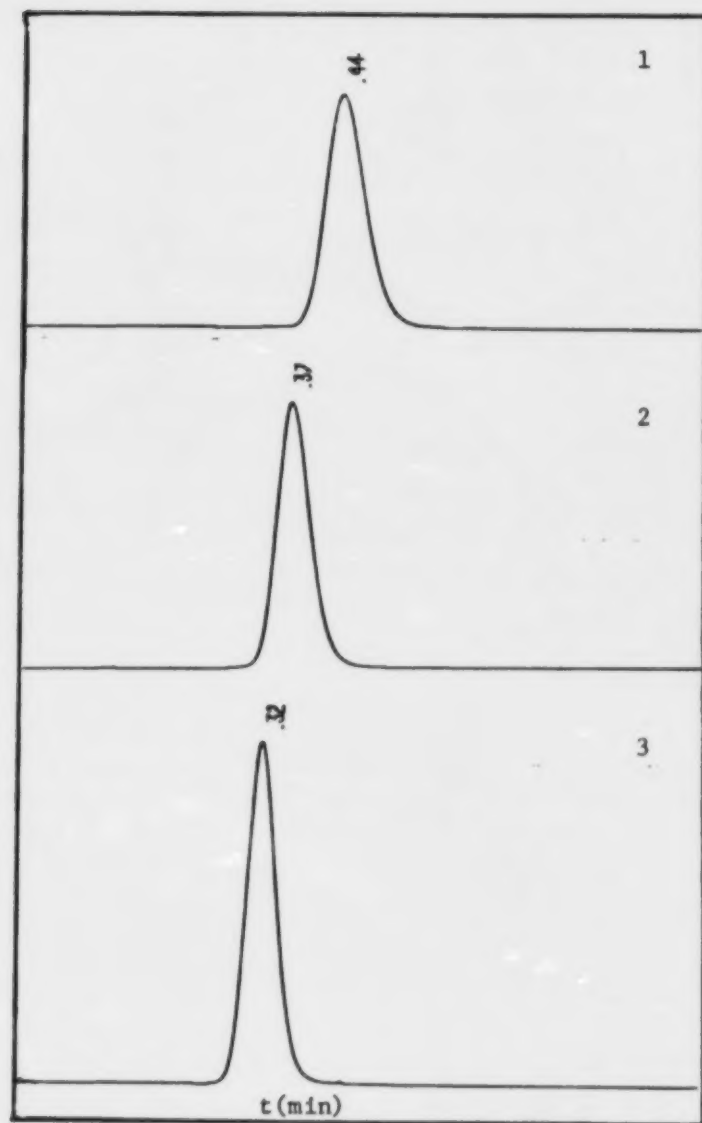


Figure III.48. Experimental chromatograms for the $N_2/Na-X$ system (Fresh bed) (30 cc/min; 0.1 mL).
1) $100^\circ C$; 2) $125^\circ C$; 3) $150^\circ C$.

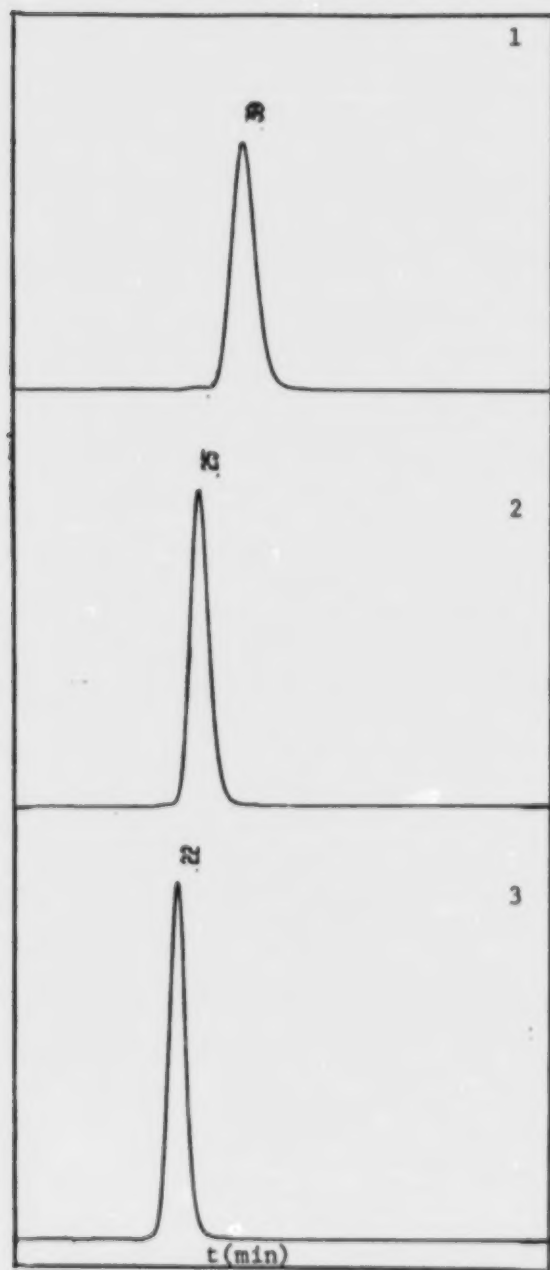


Figure III.49. Experimental chromatograms for the $N_2/Na-X$ system (Fresh bed) (45 cc/min; 0.1 mL).
1) 100°C; 2) 125°C; 3) 150°C.

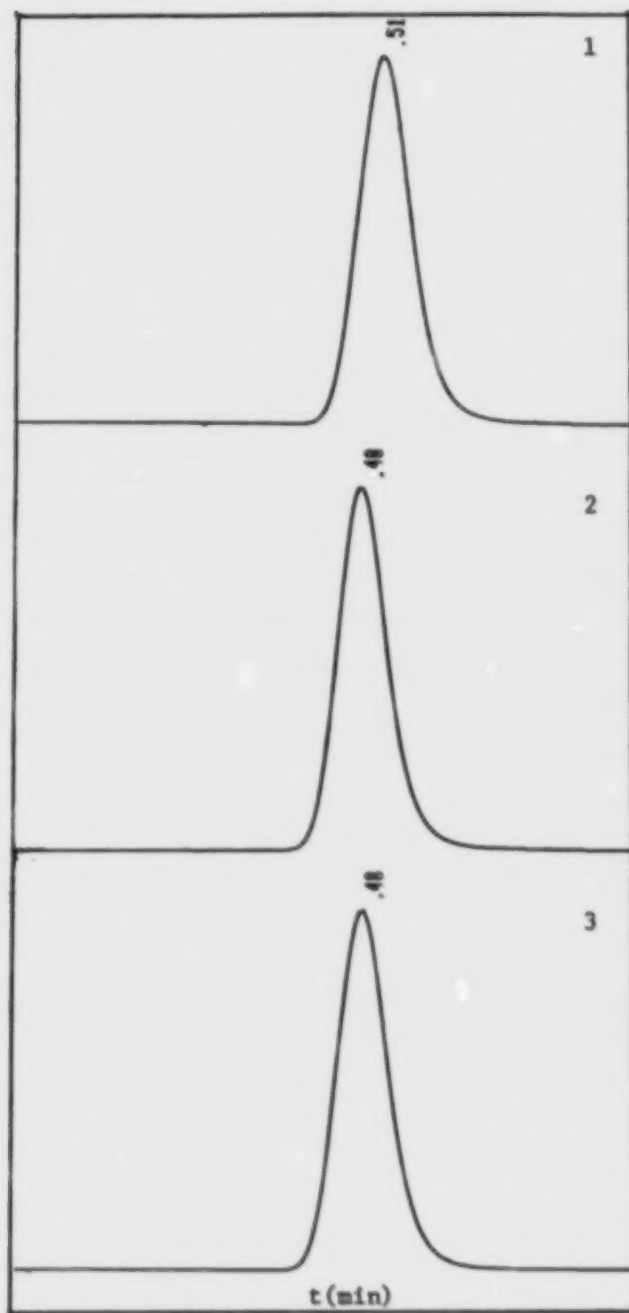


Figure III.50. Experimental chromatograms for the $N_2/Na-X$ system (Pyrrole saturated) (15 cc/min; 0.1 mL).
1) 100°C; 2) 125°C; 3) 150°C.

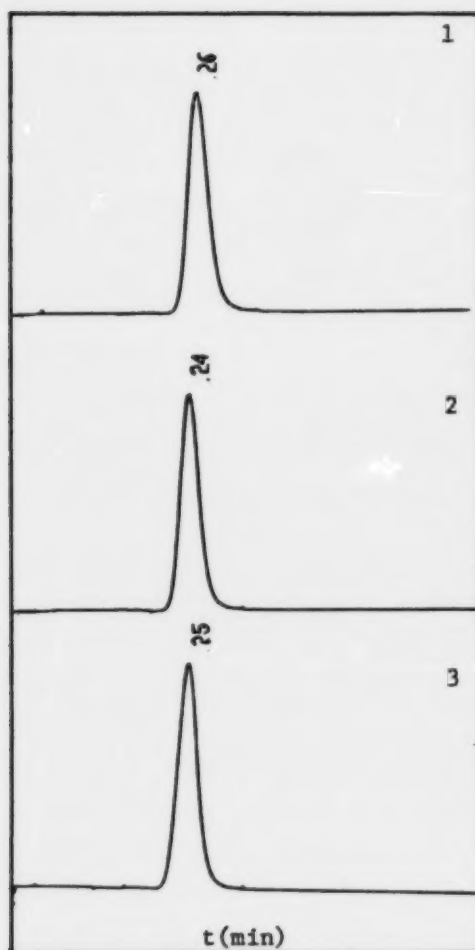


Figure III.51. Experimental chromatograms for the $N_2/Na-X$ system (Pyrrole saturated) (30 cc/min; 0.1 mL).
1) 100°C; 2) 125°C; 3) 150°C.

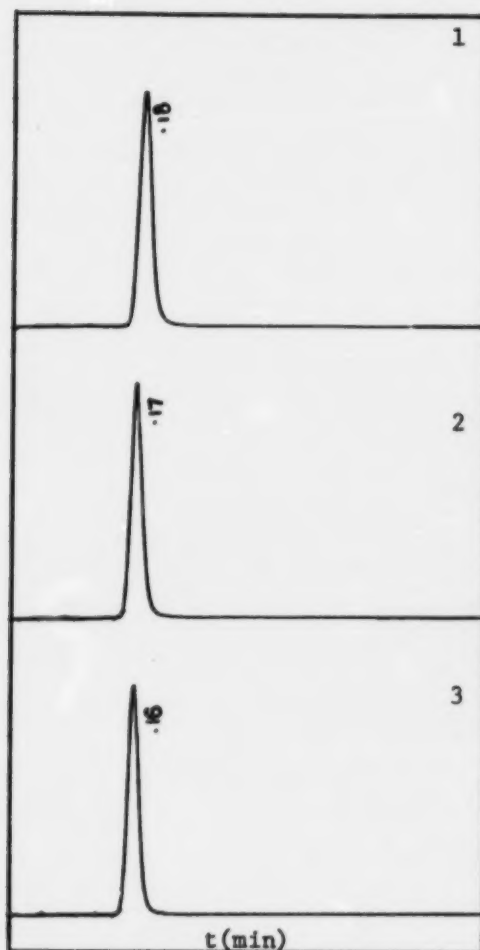


Figure III.52. Experimental chromatograms for the $N_2/Na-X$ system (Pyrrole saturated) (45 cc/min; 0.1 mL).
1) 100°C; 2) 125°C; 3) 150°C.

Bed parameters:

Weight of adsorbent : 1.35 g
 Bed length : 14.2 cm
 Particle size : 48/60 mesh
 Pulse size : 100 L

Table III.25 - Effect of pyridine saturation on the N₂ retention times in Ca-X. (Fig. III.53 - III.58)

Flow rate (cc/min)	Fresh bed			Pyridine saturated bed		
	Temperature °C			Temperature °C		
	100	125	150	100	125	150
15	0.32	0.23	0.19	0.15	0.14	0.13
30	0.16	0.12	0.10	0.08	0.07	0.07
45	0.11	0.09	0.07	0.05	0.06	0.05

Bed parameters:

Weight of adsorbent : 3.26 g
 Bed length : 32.9 cm
 Particle size : 48/60 mesh
 Pulse size : 100 L

Table III.26 - Effect of pyrrole saturation on the N₂ retention times in Ca-X. (Fig. III.59 - III.64)

Flow rate (cc/min)	Fresh bed			Pyrrole saturated bed		
	Temperature °C			Temperature °C		
	100	125	150	100	125	150
15	0.74	0.54	0.44	0.29	0.28	0.26
30	0.38	0.29	0.23	0.15	0.15	0.13
45	0.27	0.20	0.16	0.11	0.11	0.10

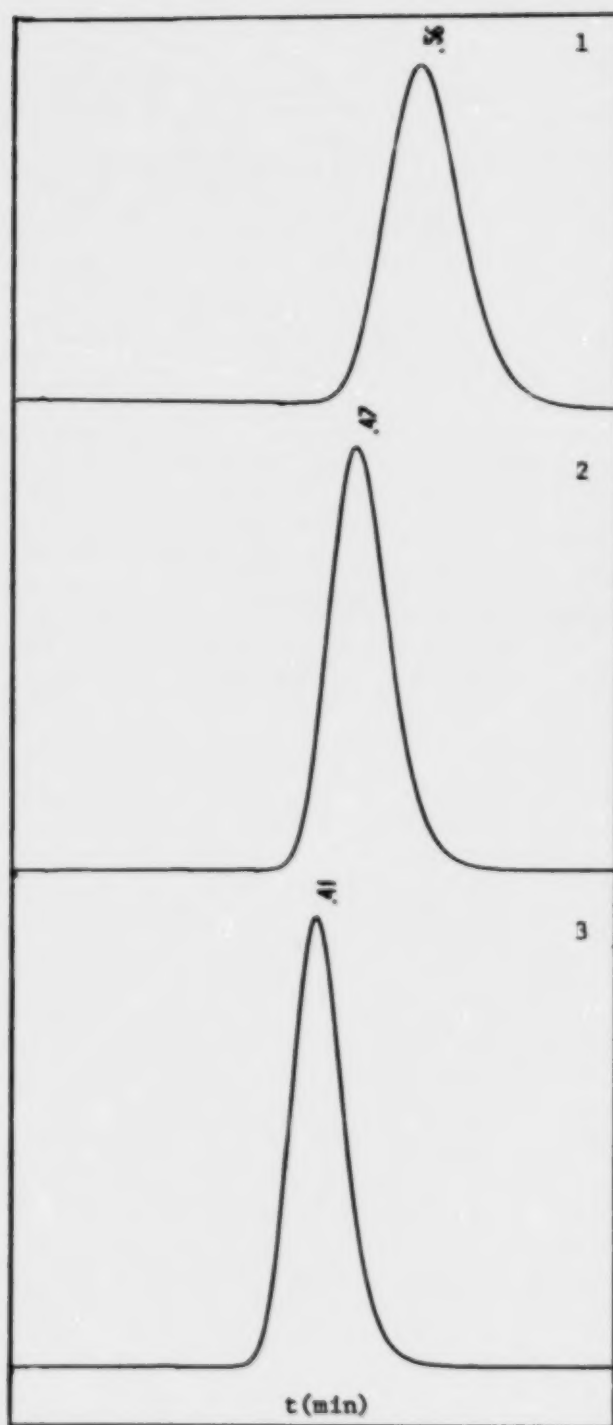


Figure III.53. Experimental chromatograms for the N_2 /Ca-X system (Fresh bed) (15 cc/min; 0.1 mL).
1) 100°C; 2) 125°C; 3) 150°C.

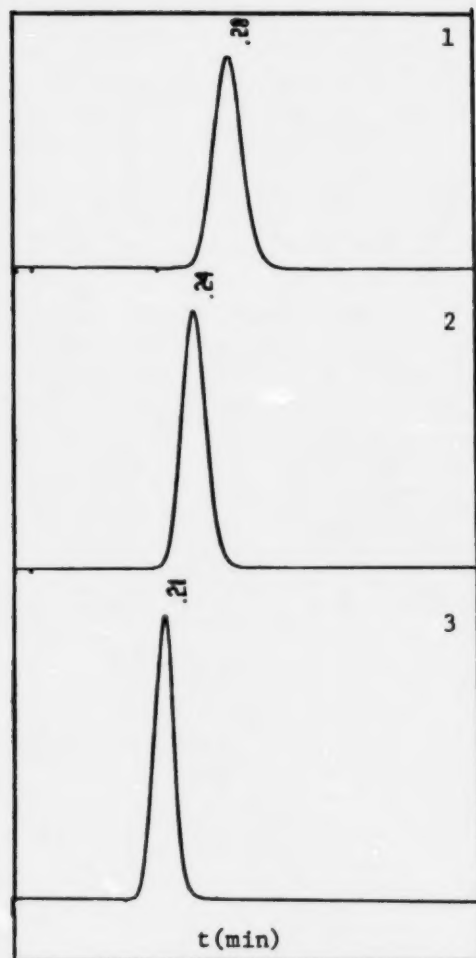


Figure III.54. Experimental chromatograms for the N_2 /Ca-X system
(Fresh bed) (30 cc/min; 0.1 mL).
1) 100°C; 2) 125°C; 3) 150°C.

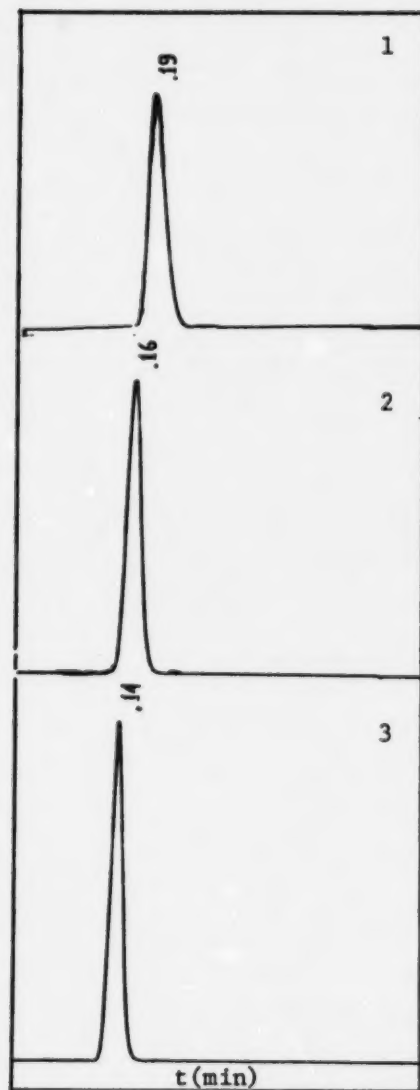


Figure III.55. Experimental chromatograms for the N_2 /Ca-X system (Fresh bed) (45 cc/min; 0.1 mL).
1) 100°C; 2) 125°C; 3) 150°C.

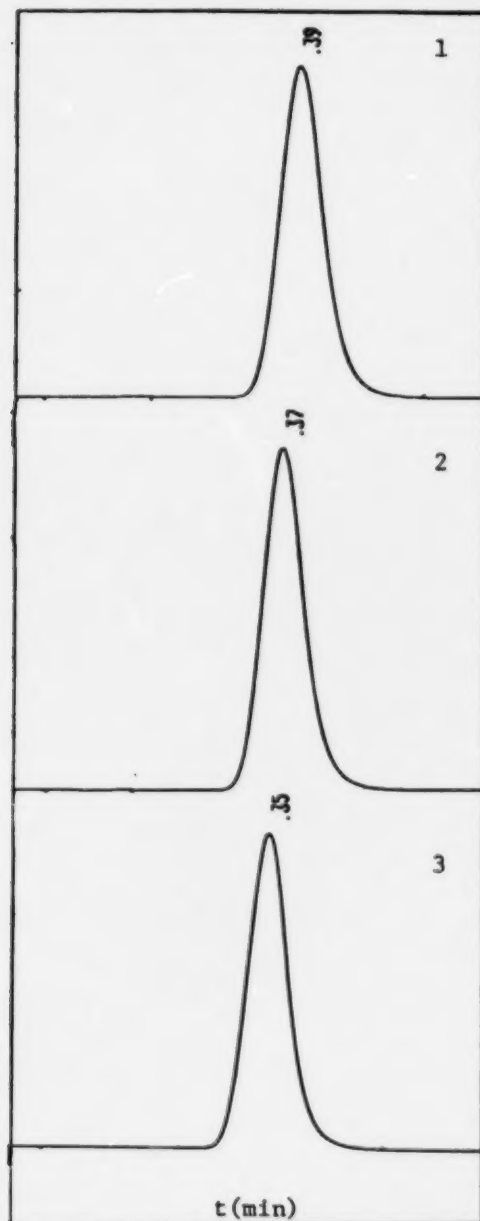


Figure III.56. Experimental chromatograms for the $N_2/Ca-X$ system (Pyridine saturated) (15 cc/min; 0.1 mL).
1) 100°C; 2) 125°C; 3) 150°C.

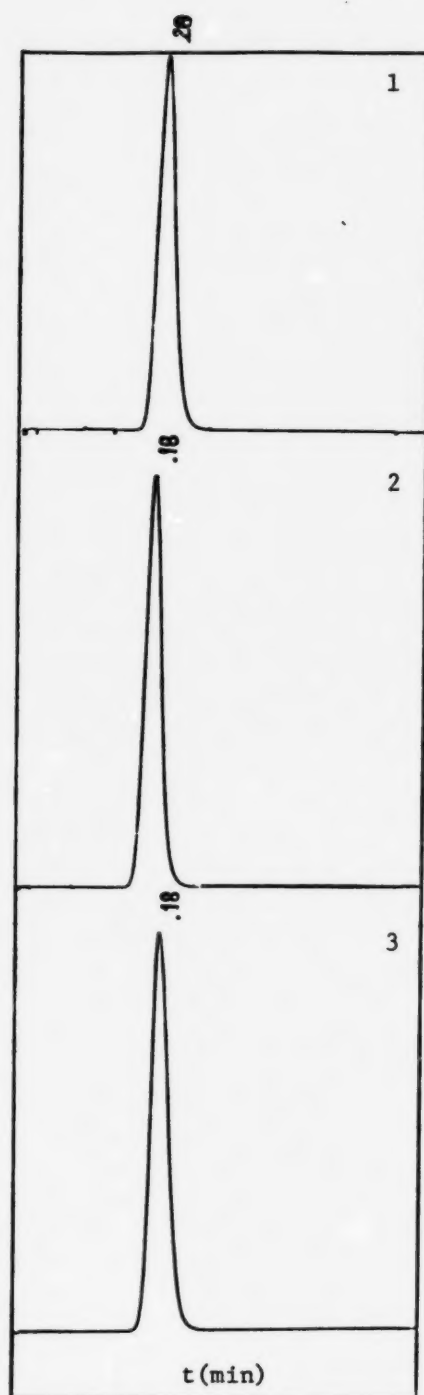


Figure III.57. Experimental chromatograms for the N_2 /Ca-X system (Pyridine saturated) (30 cc/min; 0.1 mL).
1) 100°C; 2) 125°C; 3) 150°C.

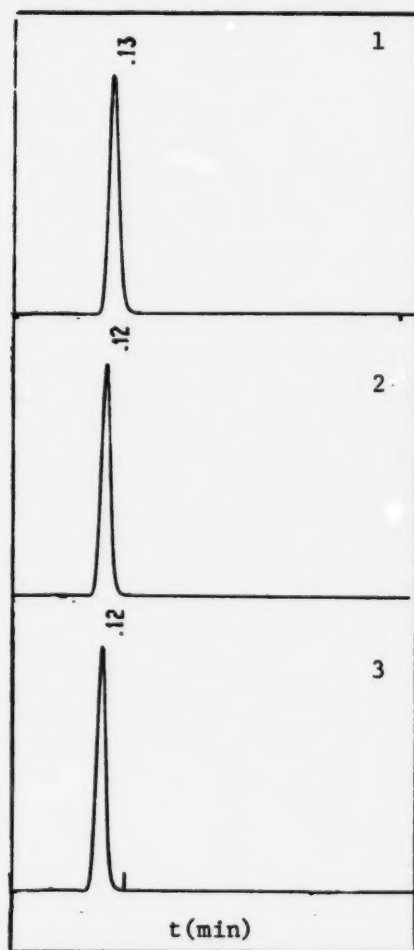


Figure III.58. Experimental chromatograms for the N_2 /Ca-X system (Pyridine saturated) (45 cc/min; 0.1 mL).
1) 100°C; 2) 125°C; 3) 150°C.

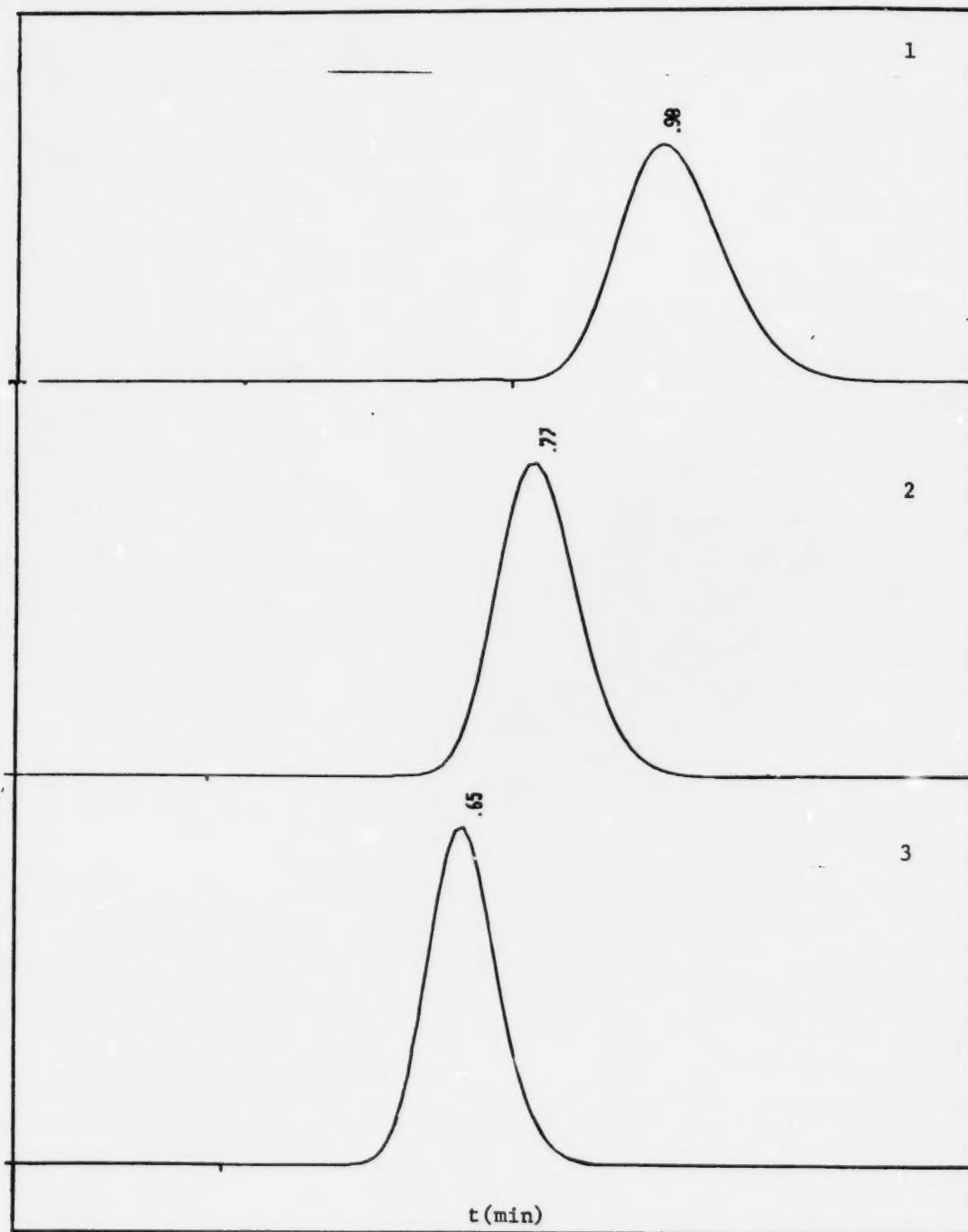


Figure III.59. Experimental chromatograms for the $N_2/Ca-X$ system (Fresh bed) (15 cc/min; 0.1 mL).
1) 100°C; 2) 125°C; 3) 150°C.

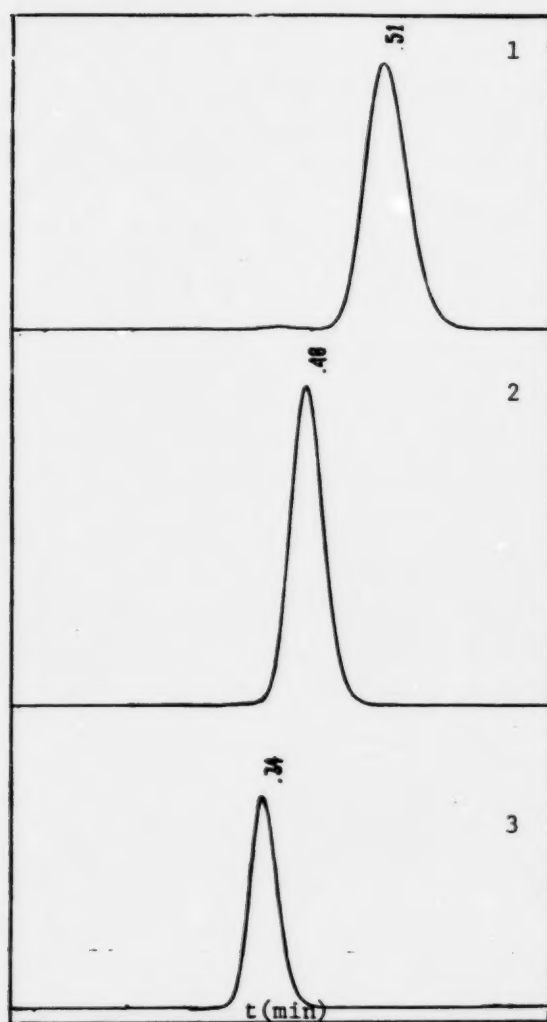


Figure III.60. Experimental chromatograms for the N_2 /Ca-X system (Fresh bed) (30 cc/min; 0.1 mL).
1) 100°C; 2) 125°C; 3) 150°C.

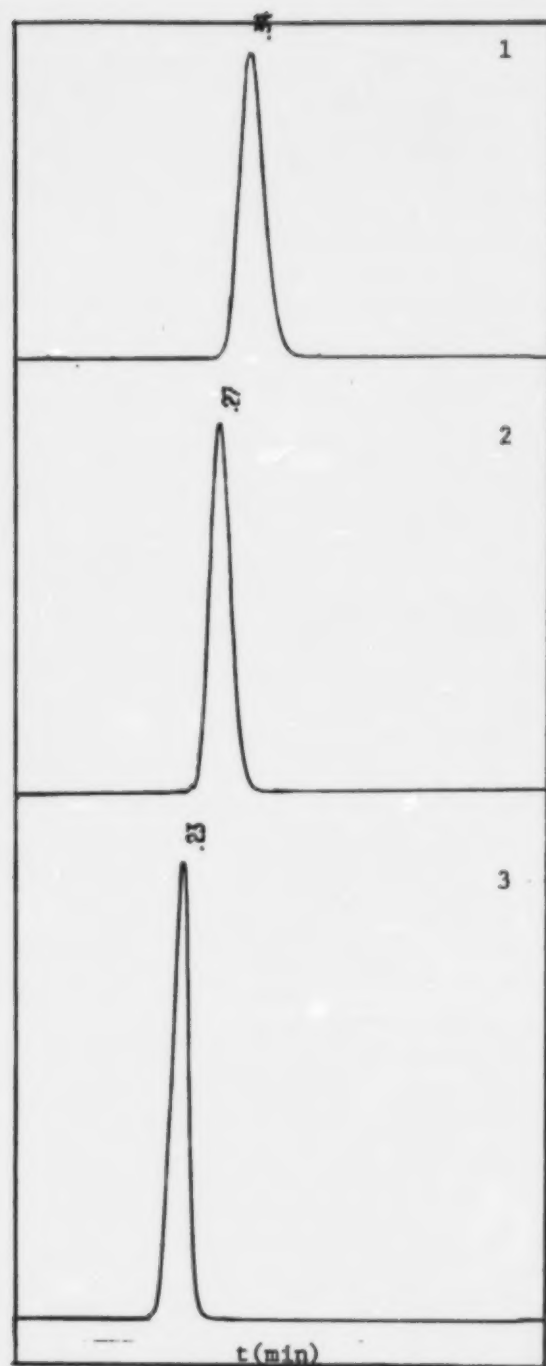
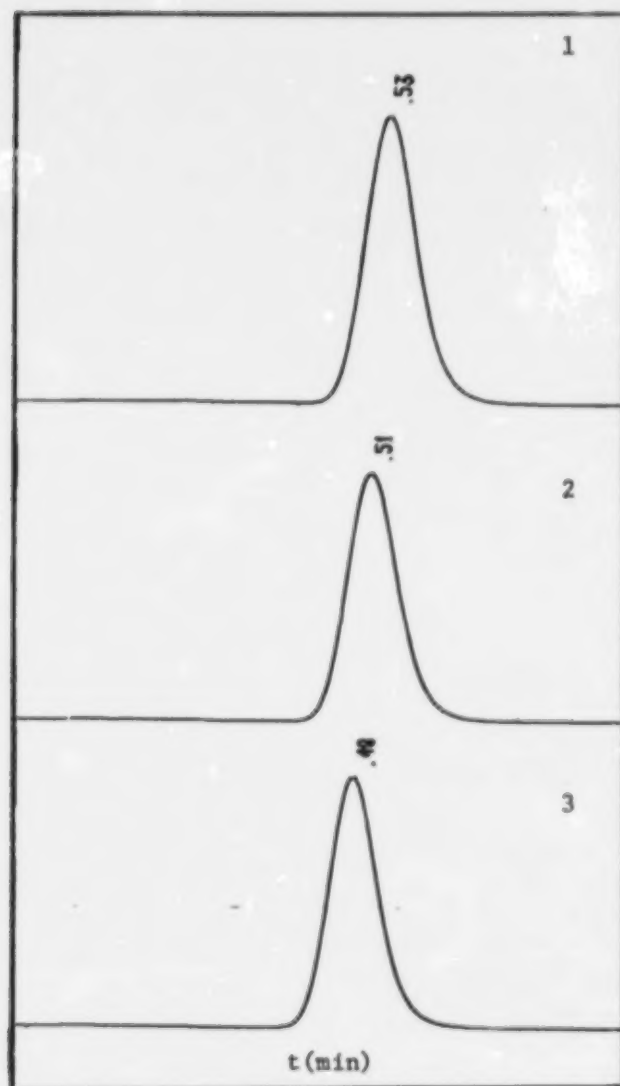


Figure III.61. Experimental chromatograms for the $N_2/Ca-X$ system (Fresh bed) (45 cc/min; 0.1 mL).
1) $100^\circ C$; 2) $125^\circ C$; 3) $150^\circ C$.



III.62. Experimental chromatograms for the N_2 /Ca-X system (Pyrrole saturated) (15 cc/min; 0.1 mL).
1) 100°C; 2) 125°C; 3) 150°C.

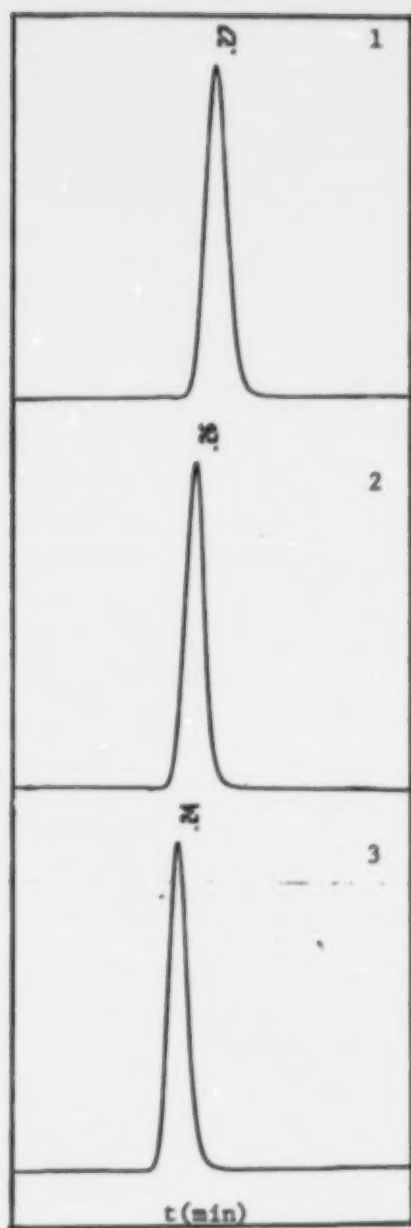


Figure III.63. Experimental chromatograms for the N_2 /Ca-X system (Pyrrole saturated) (30 cc/min; 0.1 mL).
1) 100°C; 2) 125°C; 3) 150°C.

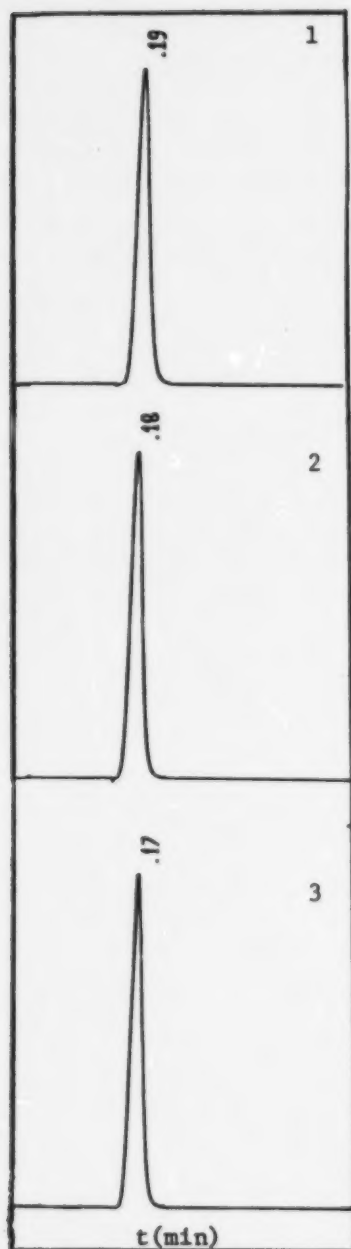


Figure III.64. Experimental chromatograms for the N_2 /Ca-X system (Pyrrole saturated) (45 cc/min; 0.1 mL).
1) 100°C; 2) 125°C; 3) 150°C.

For most of the other systems investigated (tables III.33 - III.36 and figs. III.41 - III.64) the saturation of the zeolite bed either by pyridine or pyrrole had a significant effect on the N_2 retention times at all operation conditions.

IV. ANALYSIS OF CHROMATOGRAPHIC PULSE RESPONSE DATA

As seen from the experimental data reported the behaviour of the pyridine (pyrrole)/zeolite systems are highly nonlinear. The choice of the chromatographic technique to evaluate diffusional parameters for a given adsorbate/adsorbent system is principally based on the simplicity of the technique provided that the system is linear. Most importantly, the parameter estimation techniques for linear systems applied to pulse response data are well developed (see section I.7). However, for nonlinear systems, the simplicity offered by the chromatographic technique is lost since the classical parameter estimation techniques applied to linear systems are no longer valid. Estimation of parameters for nonlinear models essentially involves the solution of governing partial differential equations by a numerical technique such as a standard finite difference, or a collocation method coupled to a nonlinear regression routine to obtain the model parameters for a best fit. Such a procedure can be realised only at the cost of a great deal of computer time.

As discussed previously the rates of adsorption and desorption in porous adsorbents are generally controlled by transport within the pore network rather than by intrinsic kinetics of sorption at the surface. The transport of molecules within pores is essentially a diffusive process and the kinetic data may be interpreted in terms of a diffusivity defined in accordance with Fick's first equation

$$J = -D(C) \frac{\partial C}{\partial x} \quad (4.1)$$

and the Fickian diffusivity D is given by the following relationship

$$D = D_0 \left(\frac{d \ln P}{d \ln C} \right) = D_0 \gamma \quad (4.2)$$

where: D_0 : corrected diffusivity

P : sorbate pressure

C : sorbate concentration

and is evaluated from empirical adsorption isotherms.

For zeolitic systems the relationship between the sorbate activity and concentration is highly nonlinear except at very low concentrations approaching the Henry's law region. At high concentrations this ratio $\frac{d \ln P}{d \ln C}$ is large and approaches infinity at the saturation region. In the Henry's law region the activity is directly proportional to the concentration. Under these conditions $\frac{d \ln a}{d \ln C} \approx 1.0$ and the diffusivity approach a constant limiting value.

Although the corrected diffusivity should be independent of the sorbate concentration within the Henry's law region (low concentration) this is not always the case always [30-33]. Ruthven and Doetsch [31] have shown that Fickian diffusivities for several hydrocarbons in NaX are concentration dependant even in the Henry's law region. According to Ruthven, when the critical molecular diameter is small in comparison to the zeolite pore dimension, the Fickian diffusivity is inversely proportional to concentration and when the molecular dimensions and pore size are comparable the Fickian diffusivity is constant.

Intracrystalline diffusivity is an activated process and the temperature dependance of the corrected diffusivity is correlated by the equation

$$D_0 = D^* e^{-E/RT} \quad (4.3)$$

where: D^* : pre exponential factor.

The activation energy is strongly dependant on the diameter of the sorbate molecule relative to the sieve window and it has been shown that for a given sorbate, the activation energy for diffusion in a 4A sieve is considerably greater than that for 5A, reflecting the effect of the differences in effective aperture [11].

The observed excessive tailing of the response signals for the pyridine (pyrrole)/zeolite systems may indicate that the spread of the response signal is determined mainly by micropore diffusional resistance. For the observed nonlinear behaviour of these systems, several reasons may be cited. a) Nonlinear isotherm effects (it has been shown that the sorption in zeolites is normally consistent with the Langmuir isotherm except at very low sorbate concentrations (Henry's law region); b) Concentration dependant corrected diffusivity; c) Nonisothermal sorption due to localized heat effects. Since chromatographic measurements are made in the presence of an excess of an inert carrier, the intrusion of heat transfer effects are expected to be insignificant, and the contribution of such effects to the system nonlinearity may be not as important as the first two possibilities.

This brief overview indicates the possible causes for the nonlinear behaviour of the investigated systems that may be incorporated into the system models. A complete description of the effect of various parameters such as the type of zeolite, type of cation on the diffusivities of pyri-

dine and pyrrole should await a solution to these systems, and the development of software applicable to nonlinear systems is presently under way. A discussion on the development of the software is followed herein.

IV.1 MATHEMATICAL MODELS

The chromatographic method of measuring mass transfer and diffusional resistances in porous adsorbents consists of matching the experimental chromatogram to a theoretical response curve predicted from an appropriate dynamic model. The dynamic behaviour of a chromatographic column according to the Kubin-Kucera model is represented by the following set of differential equations:

in the column:

$$\frac{\partial C_z}{\partial t} = D_{ax} \frac{\partial^2 C}{\partial z^2} - v \frac{\partial C_z}{\partial z} - \frac{3D_e}{R} \cdot \frac{1 - \epsilon_b}{\epsilon} \left(\frac{\partial C_p}{\partial r} \right)_{r=R} \quad (4.4)$$

in the particle:

$$D_e \left(\frac{\partial^2 C_p}{\partial r^2} + \frac{2}{r} \frac{\partial C_p}{\partial r} \right) - \epsilon_p \frac{\partial C_p}{\partial t} - \rho_p \frac{\partial C_{ad}}{\partial t} = 0 \quad (4.5)$$

For example: a) rate of adsorption is linear;

$$\frac{\partial C_{ad}}{\partial t} = k_a \left(C_p - \frac{C_{ad}}{K_A} \right) \quad (4.6)$$

b) rate of adsorption is nonlinear

$$\frac{\partial C_{ad}}{\partial t} = k'_a \left[C_p (C_{ad,max} - C_{ad}) - \frac{C_{ad}}{K'_A} \right] \quad (4.7)$$

with:

$$C_z(z, 0) = 0 \quad (4.8)$$

$$C_z(0, t) = f(t) \quad (4.9)$$

$$\frac{\partial C_z}{\partial z}(\infty, t) = 0 \quad (4.10)$$

$$C_p(r, z, 0) = C_{ad}(r, z, 0) = 0 \quad (4.11)$$

$$\frac{\partial C_p}{\partial r}(0, z, t) = 0 \quad (4.12)$$

$$D_e \frac{\partial C_p}{\partial r} \Big|_{r=R} = K_f \left(C_z - C_p \Big|_{r=R} \right) \quad (4.13)$$

If the adsorption rate is very fast, the adsorbed phase concentration of the adsorbent may be assumed to be in equilibrium with the fluid phase concentration at any instant. In such a situation the equations (4.6) or (4.7) should be replaced by the corresponding isotherm equations.

For example: a) linear isotherm;

$$C_{ad} = K_A C_p \quad (4.14)$$

b) Langmuir isotherm;

$$\frac{C_{ad}}{C_{ad,max}} = \frac{K'_A C_p}{1 + K'_A C_p} \quad (4.15)$$

The Kubin-Kucera model however does not take into account the bi-dispersed pore structure of most commercial adsorbents which generally consist of small microporous particles (such as zeolite crystals) formed into macroporous pellets with a clay binder or by compacting the zeolite crystals under pressure. In such adsorbents there are three distinct resistances to mass transfer associated with diffusion through the external fluid film, the pellet macropores, and the crystal micropores. A suitable mathematical model for such a system was developed by Haynes and Sarma [34] and is used widely.

The data processing methods that are commonly used for the analysis of chromatographic pulse response data are discussed in detail in section I.7. These methods are however, only applicable to linear systems, and hence cannot be used to extract transport parameters from the chromatographic pulse response data obtained for nitrogen compounds/zeolite systems. These systems were shown to be highly nonlinear (section IV). For this reason a numerical method for the estimation of parameters was developed. The developed parameter estimation technique is based on the method of finite differences to solve the governing partial differential equations and is coupled to a nonlinear least squares curve fitting routine. Initially the numerical methodology was developed for the Kubin-Kucera model [equations (4.4) - (4.13)] for the case where the rate of adsorption is linear. It should however, be mentioned that although, the computer programs were initially developed to handle linear systems, these could be quite easily modified to handle system nonlinearities. This method also could be modified to take into account the bidispersed pore structure of the commonly used adsorbents. The developed computer software was implemented on a Control Data CYBER 80-830 computer.

IV.2 ESTIMATION OF PARAMETERS BY THE METHOD OF MOMENTS

For linear models a rough estimate of the transport parameters may be obtained using the moment method as proposed by Kubin [13] and Kucera [14]. These parameter values then may be used as initial guesses and be updated by using the parameter optimization technique proposed in the text.

Kubin [13] and Kucera [14] showed that, in principle, the five parameters (D_{ax} , D_e , k_f , k_a , and K_A) involved in the model equations for the case with first order reversible adsorption [equations (4.4) - (4.13)] are determinable by taking up to the fifth moments from a single response curve. However, in practice, higher moments have magnified errors and it is not feasible to determine so many parameters from a single measurement.

The parameter estimation method proposed by Schneider and Smith [35], instead, is based on the evaluation of the first and second moments from a series of measurements with various flow rates.

The difference between the theoretical first moments of the response and input signals for the Kubin-Kucera model is:

$$M_1^R - M_1^I = \frac{L}{V} (1 + \delta_0) \quad (4.16)$$

where:

$$\delta_0 = \frac{(1 - \epsilon_b)}{\epsilon_b} [\epsilon_p + \rho_p K_A] \quad (4.17)$$

Likewise, the difference between the second central moments of the response and input signals is:

$$\mu_2^R - \mu_2^I = \frac{2L}{V} \left[\delta_1 + \frac{D_{ax} (1 + \delta_0)^2}{V^2} \right] \quad (4.18)$$

where:

$$\delta_1 = \frac{(1 - \epsilon_b)}{\epsilon_b} \left[\frac{\rho_p (K_A)^2}{k_a} + (\epsilon_p + \rho_p K_A)^2 \left(\frac{1}{5D_e} + \frac{1}{k_f R} \right) \frac{R^2}{3} \right] \quad (4.19)$$

According to the Schneider and Smith's method, the transport parameters are evaluated from the plots of $(M_1^R - M_1^I)$ vs. L/V and $(\mu_2^R - \mu_2^I) V/2L$ vs. V^{-2} for a series of measurements at various flow rates. The K_A value is estimated from the slope of the straight line plot $(M_1^R - M_1^I)$ vs. L/V . The values δ_1 and D_{ax} are obtained from the slope and the intercept of the plot $(\mu_2^R - \mu_2^I) V/2L$ vs. V^{-2} . The analysis is based on the assumption that both D_{ax} and k_f are not influenced by u and this assumption is satisfied if measurements are made at low flow rates.

The value of D_e can be obtained from δ_1 if the values of k_a and k_f are known. In the present work the k_f was calculated from the correlation (4.20) given in reference [23], and k_a was assumed to be infinite (equilibrium kinetics).

IV.2.1 Estimation of the film mass transfer coefficient (k_f)

The value of k_f was determined using the following correlation [23].

$$N_{sh} = 2 + 1.1 N_{sc}^{1/3} N_{Re}^{0.6} \quad (3 < Re < 3000) \quad (4.20)$$

where:	dimensionless number	definition
	Sh	Sheerwood
	Sc	Schmidt
	Re	Reynolds

$$\frac{2K_f R}{D_v}$$

$$\frac{\mu}{\rho_f D_v}$$

$$\frac{2R V \rho_f}{\mu}$$

The molecular diffusion coefficient was estimated from the correlation given below [23].

$$D_v = \frac{6.7 \times 10^{-8} T^{1.83} \left(\frac{1}{MW_1} + \frac{1}{MW_2} \right)}{P \left[\left(\frac{T}{P} \frac{c_1}{c_1} \right)^{1/3} + \left(\frac{T}{P} \frac{c_2}{c_2} \right)^{1/3} \right]} \quad (4.21)$$

where: D_v : molecular diffusion coefficient (m^2/s)

MW_i : molecular weight of gas i

P : pressure (atm)

P_{ci} : critical pressure of the gas i (atm)

T : temperature (K)

T_{ci} : critical temperature of the gas i (K).

The gas viscosity μ was determined by first considering the effect of temperature for each component. A correlation given by Perry [36] was used:

$$\mu_i = \frac{k_i T^{3/2}}{T + 1.47 T_{B1}} \quad (4.22)$$

where: μ : viscosity (kg/ms)

k_i : is a constant

T_{B1} : is the boiling point of component i (K)

T : is the temperature (K).

Then the viscosity of low pressure gas mixtures may be calculated from the component viscosities according to the Nerning-Zipperer correlation [36] given by:

$$\mu = \frac{\sum y_i \mu_i (MW_i)^{1/2}}{\sum y_i (MW_i)^{1/2}} \quad (4.23)$$

where: y_i : mole fraction of component i .

IV.3 FINITE DIFFERENCE SOLUTION OF MODEL EQUATIONS

A finite difference scheme attempts to represent a time-space continuum by a set of discretely spaced points, which are referred to as the mesh, grid or node points. These mesh points are superimposed upon the continuum and attention is focused to these points only. Finite difference methods approximate differential equations through algebraic representations of derivatives at the mesh points in the continuum.

A finite difference representation of the Kubin-Kucera model has been developed in this work. In the development, special care was taken in the choice of the finite difference representation of the derivatives. The finite difference representation of the bulk gas mass balance and the pore volume mass balance equations are given in tables IV.1 and IV.2 respectively.

The accumulation terms for the bulk gas and pore volume mass balances are represented by a linear Euler finite differences for the first time step since only concentrations from the previous time step (i.e. the ini-

Table IV.1 - Finite difference representations for the column bulk gas mass balance.

Term	Representation	Order of truncation error	Name
Accumulation: $\frac{\partial C}{\partial t}$	$\frac{C_{ij} - C_{ij-1}}{\Delta t}$	$O(\Delta t)$	Euler
	$\frac{3C_{ij} - 4C_{ij-1} + C_{ij-2}}{2\Delta t}$	$O(\Delta t^2)$	Gear
Convection: $\frac{\partial C}{\partial z}$	$\frac{C_{ij} - C_{i-1,j}}{\Delta z}$	$O(h)$	Upwinded
Dispersion: $\frac{\partial^2 C}{\partial z^2}$	$\frac{C_{i+1,j} - 2C_{ij} + C_{i-1,j}}{\Delta z^2}$	$O(h^2)$	2nd derivative
Boundary condition: $\left(\frac{\partial C}{\partial z}\right)_{z=L}$	$\frac{3C_{N,j} - 4C_{N-1,j} + C_{N-2,j}}{2\Delta z}$	$O(h^2)$	Centered @ $C_{N,j}$

Table IV.2 - Finite difference representations for the adsorbent particle gas phase mass balance.

Term	Representation	Order of truncation error	Name
Accumulation: $\frac{\partial C}{\partial t}$	$\frac{(C)_{i,j} - (C)_{i,j-1}}{\Delta t}$	$O(\Delta t)$	Euler
	$\frac{3(C)_{i,j} - 4(C)_{i,j-1} + (C)_{i,j-2}}{2\Delta t}$	$O(h^2)$	Gear
Diffusion: $\frac{\partial C}{\partial r}$	$\frac{(C)_{i+1,j} - (C)_{i-1,j}}{\Delta r_i}$	$O(h)$	Variable mesh
$\frac{\partial^2 C}{\partial r^2}$	$\frac{(C)_{i+1,j} - (C)_{i,j} - \frac{(C)_{i,j} - (C)_{i-1,j}}{\Delta r_i}}{\frac{\Delta r_{i+1} + \Delta r_i}{2}}$	$O(h^2)$	
Boundary condition: $\left(\frac{\partial C}{\partial r}\right)_{r=0}$	$\frac{4(C)_{2,j} - 2(C)_{1,j} - 3(C)_{0,j}}{\Delta r_1 + \Delta r_2}$	$O(h^2)$	Centered @ $(C)_0$
Boundary condition: $\left(\frac{\partial C}{\partial r}\right)_{r=R}$	$\frac{3(C)_{M,j} - 4(C)_{M-1,j} + 2(C)_{M-2,j}}{\Delta r_{M-1} + \Delta r_M}$	$O(h^2)$	Centered @ $(C)_M$

tial conditions) are required. A better representation of the accumulation terms, however, is through a Gear finite difference which requires concentrations from two previous time steps; so, a Gear finite difference cannot be used until the second time step. The advantage in using the Gear finite difference is that it is centred at the current time step whereas the Euler finite difference is centred between the previous and current time steps [37]. The Gear finite difference renders the resolution of the finite difference scheme more stable and thus larger time steps can be employed (fig. IV.1).

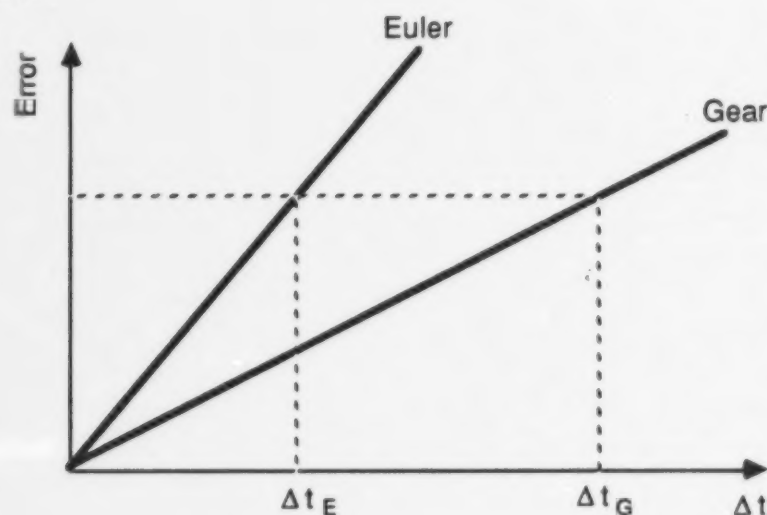


Figure IV.1. Relationship between the error and the stepsize for the Euler and gear schemes.

In using finite difference representations such as those of Euler and Gear for the time derivatives, implicit methods are necessary [37] to resolve the finite difference equations. Implicit methods are attractive since they avoid the necessity of using extremely small time steps which are required for explicit methods.

The finite difference for the convection term in the bulk gas mass balance is a backward difference since a central difference can lead to stability problems [37].

For the boundary condition (4.10) at the column exit, a finite difference approximation without using fictitious grid points is used where the finite difference is centred at the column exit. This representation is very similar to that of the Gear finite difference for the accumulation term.

Likewise, similar finite differences are used for the particle boundary conditions (4.12) and (4.13) where the finite difference is centred at the centre and radius of the particle.

The finite difference representations for the Kubin-Kucera adsorption model result in a grid form involving approximations at the points shown below for either the bulk gas or particle representation.

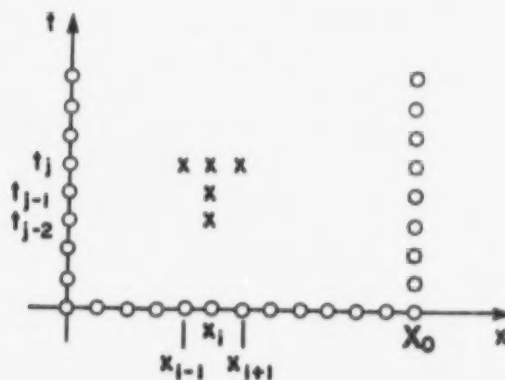


Figure IV.2. Finite difference grid.

Of course, the t_{j-2} grid point is not required when the time derivative is expressed as a Euler finite difference. To determine the concentrations at the j^{th} time step, implicit methods using matrix algebra are required [38].

The implicit finite difference representation of both mass balance equations yield a tridiagonal symmetrical matrix system. The solution of such systems can be done either by Crout Reduction of the tridiagonal system or by the SOR technique [38]. Crout Reduction, however, is generally acceptable unless the number of nodes is very large.

The typical tridiagonal matrix system to be solved for the finite difference scheme is summarized below:

$$[A] C_j = W \quad (4.24)$$

where:

$$W = \begin{cases} f(C_{1,j-1}) & \text{Euler} \\ f(C_{1,j-1}, C_{1,j-2}) & \text{Gear} \end{cases}$$

$$A = \begin{bmatrix} & & & \\ & & & \\ & & & \\ & & & \end{bmatrix}$$

which can be resolved by the method of Crout Reduction.

The method of Crout Reduction involves the factorization of the square matrix, A , of size M into the triangular matrices L and U . Since matrix A is tridiagonal, the storage of its elements can be in terms of the vectors a , b and c as shown below:

$$[A] = \begin{bmatrix} b_1 & c_1 & & \\ a_1 & b_2 & c_2 & \\ & a_2 & b_{n-1} & c_{n-1} \\ & & a_{n-1} & b_n \end{bmatrix} = \begin{bmatrix} L_{11} & 0 & 0 & 0 \\ L_{21} & L_{22} & 0 & 0 \\ 0 & L_{32} & L_{33} & 0 \\ 0 & 0 & L_{43} & L_{44} \end{bmatrix} \begin{bmatrix} 1 & u_{12} & 0 & 0 \\ 0 & 1 & u_{23} & 0 \\ 0 & 0 & 1 & u_{34} \\ 0 & 0 & 0 & 1 \end{bmatrix}$$

where the elements in L and U can be stored in A.

Thus the factorized matrix can be computed according to [38].

$$\begin{array}{rcl}
 b_1 & = & b_1 \\
 c_1 & = & c_1/b_1 \\
 \left. \begin{array}{l} b_i & = & b_i - a_{i-1} * C_{i-1} \\ C_i & = & C_i/b_i \\ a_i & = & a_i \end{array} \right\} & & 2 \leq i \leq n-1 \\
 b_n & = & b_n - a_{n-1} * C_{n-1} \\
 a_{n-1} & = & a_{n-1}
 \end{array}$$

IV.4 PARAMETER OPTIMIZATION TECHNIQUES

IV.4.1 General techniques

Numerous optimization techniques are available in the literature, each being applicable to certain types of problems. All techniques, however, can be categorized as either an exhaustive enumeration, an indirect or a direct method. As the term optimization suggests, an objective function to be optimized is either minimixed or maximized depending upon the nature of the problem at hand. The concept of optimization can be thought of as [39]:

$$Y(X^*) = Y^* = \text{Opt}[Y(X)] \quad (4.25)$$

where: Y^* : is either the maximum or minimum of the objective function Y

X^* : is where the optimum occurs.

The exhaustive enumeration technique involves evaluating the objective function at a finite number of possibilities (X's) and picking out the

optimum directly. This technique is also known as the brute force approach. This is a satisfactory technique only if the number of possibilities is rather small and the computation of the objective function is relatively easy [39]. Otherwise, better techniques are required.

Indirect optimization methods are very economical when they can be applied since they involve solving an equation rather than searching for an optimum. These techniques are applicable when the objective function is known analytically or if approximation techniques are used. In the latter, one evaluates the objective function at many points to approximate it by an expression amenable to indirect methods. For indirect methods, the differential approach is used whereby the optimum is located where the first derivatives vanish. Approximation techniques can also be very costly since the objective function must be evaluated a number of times to accurately approximate it by a polynomial.

Direct optimization methods on the other hand can be classified as either a direct elimination technique or a direct climbing procedure. The former uses bold moves to shrink the region in which the optimum must lie while the latter, often referred to as gradient techniques, cautiously move in the direction where the objective appears to be improving based on local measurements [39]. The method of least squares is a special type of gradient method which takes into account the particular nature of the objective function.

IV.4.2 Least squares method

The objective function for the method of least squares is defined as the sum of the squares of a set of functions. The least squares problem requires the objective function:

$$y(X) = \sum_{i=1}^M \phi_i(X)^2 ; X \in R^N \quad (4.26)$$

to be minimized [40], where:

X : is the vector of optimization parameters

M : is the size of X

N : is the number to data points to be fitted

$\phi_i(X)$: is the residual function defined as:

$$\phi_i(X) = f(X_i, \beta) - Y_i(\beta) \quad (4.27)$$

where:

$f(X_i, \beta)$: is the model function which is a function of X and

$Y_i(\beta)$: is the function to fit the model to

β : is the independant variable.

In the case of fitting a model to an experimental curve, $\phi_i(X)$ represents the difference between a predicted and an observed value at a given time (β). If the model function is linear in X , then the least squares problem is linear; otherwise, it is nonlinear.

The nonlinear least squares problem can be solved by two classes of methods. The first class uses an affine model, $M_c(X)$, of (X_c) around X_c [40] given by:

$$M_c(X) = \phi(X_c) + J(X_c) (X - X_c) \quad (4.28)$$

where: X_c : is vector of current parameter values

$J(X_c)$: is the Jacobian matrix defined as:

$$J(X)_{ij} = \frac{2\phi_1(X)}{2X_j} \quad (4.29)$$

For the case where $M = N$, $M_c(X)$ can be driven to zero; but where $M > N$ the system is overdetermined and $M_c(X)$ can only be minimized. Methods which involve equation (4.28) are known as Gauss-Newton-type methods.

The second class of methods uses a full Taylor-series quadratic model of $f(X)$ around X_c which is given by:

$$\begin{aligned} M_c(X) = & 1/2 R(X_c)^T R(X_c) + R(X_c)^T J(X_c)(X - X_c) + \\ & 1/2 (X - X_c)^T [J(X_c)^T J(X_c) + S(X_c)] (X - X_c) \end{aligned} \quad (4.30)$$

where:

$$S(X_c) = \sum_{i=1}^m \phi_1(X_c) \nabla^2 \phi_1(X_c) \quad (4.31)$$

Methods which involve equation (4.30) are classified as full-Newton-type methods.

Dennis and Schnabel [40] discussed the relative advantages and disadvantages of the Gauss-Newton methods. The advantages are that they are locally quadratically convergent on zero residual problems and are quickly locally linearly convergent on problems which aren't too nonlinear and have reasonably small residuals. They also solve linear least squares problems in one iteration.

The disadvantages are that the methods are slowly locally convergent on sufficiently nonlinear or large residual problems and are not convergent at all for very nonlinear or very large residual problems. The methods also are not well defined if the Jacobian does not have full column rank and may not converge globally.

On the other hand, Newton methods have much superior convergence properties for almost all problems. The disadvantage of the Newton methods is that they require an approximation of the second derivative matrix which must be approximated by finite differences which is usually prohibitive in cost. Thus Newton methods are rarely used in practice [40].

The classical solution to equation (4.28) is:

$$X_+ = X_c - (J(X_c)^T J(X_c))^{-1} J(X_c)^T \phi(X_c) \quad (4.32)$$

where: X_+ : is the vector of new values of the optimization parameters.

The iterative method consists of using equation (4.32) at each iteration until a specified convergence criterion is met.

Solution of equation (4.32) directly can cause underflows and overflows and can square the conditioning of the problem in comparison to a method which uses $J(X_c)$ directly [40]. If $J(X_c)$ has full column rank, it can be decomposed by a QR factorization.

$$\begin{matrix} n \\ \boxed{J^T} \\ m \end{matrix} = \begin{matrix} m \\ \boxed{Q} \\ m \end{matrix} \times \begin{matrix} n \\ \triangle R \\ n \end{matrix} \quad (4.33)$$

The technique for converting the n column vectors of J^T , denoted as a_i , can be converted into a set of orthogonal vectors by the Gram-Schmidt process. First $V_1 = a_1$, then each V_i is orthogonal to the preceeding $V_1 \dots V_{i-1}$ according to:

$$V_i = a_i - \frac{V_1^T a_i}{V_1^T V_1} V_1 - \dots - \frac{V_{i-1}^T a_i}{V_{i-1}^T V_{i-1}} V_{i-1} \quad (4.34)$$

The vectors, V_i , may then be made orthonormal by:

$$q_i = \frac{V_i}{\|V_i\|} \quad (4.35)$$

where: q_i : are the orthonormal column vectors in Q

$\|V_i\|$: is the l_2 norm of V_i .

The upper triangular matrix R can then determined by:

$$\begin{aligned} R_{ij} &= \|V_i\| \\ R_{ij} &= \alpha_{ij} \|V_i\| \quad j > i \end{aligned} \quad (4.36)$$

where:

$$\alpha_{ij} = \frac{V_i^T a_j}{V_i^T V_i} \quad (4.37)$$

The iterative least squares problem then becomes:

$$X_+ = X_c + R^{-1} (X_c)^T Q^T (X_c) \phi (X_c) \quad (4.38)$$

The Jacobian matrix is approximated through finite differences when $f(X, \beta)$ cannot be expressed analytically. Often $f(X, \beta)$ is expensive to eva-

luate and thus other numerical approximations to the Jacobian matrix are sought. One such technique is that of using secant approximations.

The most successful secant method extension has been the Broyden update [40], where the Jacobian matrix is updated according to:

$$J(X_i) = J(X_{i-1}) + A_i \quad (4.39)$$

where Broyden suggested:

$$A_i = A_{i-1} + \frac{(Y_i - A_{i-1} \Delta X_i)(\Delta X_i)^T}{(\Delta X_i)^T \Delta X_i} \quad (4.40)$$

At least for the first iteration, one is obligated to use finite differences to approximate the Jacobian matrix.

IV.5 PARAMETER ESTIMATION ALGORITHM

Software was developed for the Kubin-Kucera adsorption model with linear-equilibrium adsorption kinetics using a finite difference scheme to solve the differential equations and a nonlinear optimization routine to determine the correct physical parameter values. The algorithm is summarized in figure IV.3.

First, it is necessary to initialize both the resolution and physical parameter values for a given experiment. The parameter values are stored in a datafile, which may be edited if the parameter values are to be altered.

For linear systems, the adsorption equilibrium constant, the effective intraparticle diffusivity and the axial dispersion coefficient can be

estimated through the method of moments. The mass transfer coefficient on the other hand can be estimated by a correlation such as equation (4.20).

Estimates for the physical parameters for nonlinear systems are, however, more difficult. The axial dispersion coefficient can be estimated using the method of moments for an adsorption system using nitrogen as the adsorbate. The effective diffusivity and the mass transfer coefficient can be estimated by correlations. The maximum adsorbed concentration can be estimated from temperature programmed adsorption studies; but simply, there is no technique available for estimating the adsorption equilibrium constant. Thus a value must be assumed in hope that it will be sufficiently close to the correct value to enable convergence.

In order to fit the calculated response curve to the experimental curve, a number of curve points are chosen on the experimental curve for fitting purposes. The selection of curve points in the tail portion of the response curve is avoided since the errors are largest here. The curve points for fitting of the response curves are stored in another datafile, which again can be edited.

The initial conditions ($C_B = C_P = C_R = 0$) are set to zero before commencing the finite difference resolution. Then the bulk gas concentrations are computed based on the initial conditions using a Euler finite difference for the time derivative. The concentration profiles are computed next within particles having a minimum significant bulk gas concentration surrounding them (CBMIN). The number of particles surrounded by CBMIN is

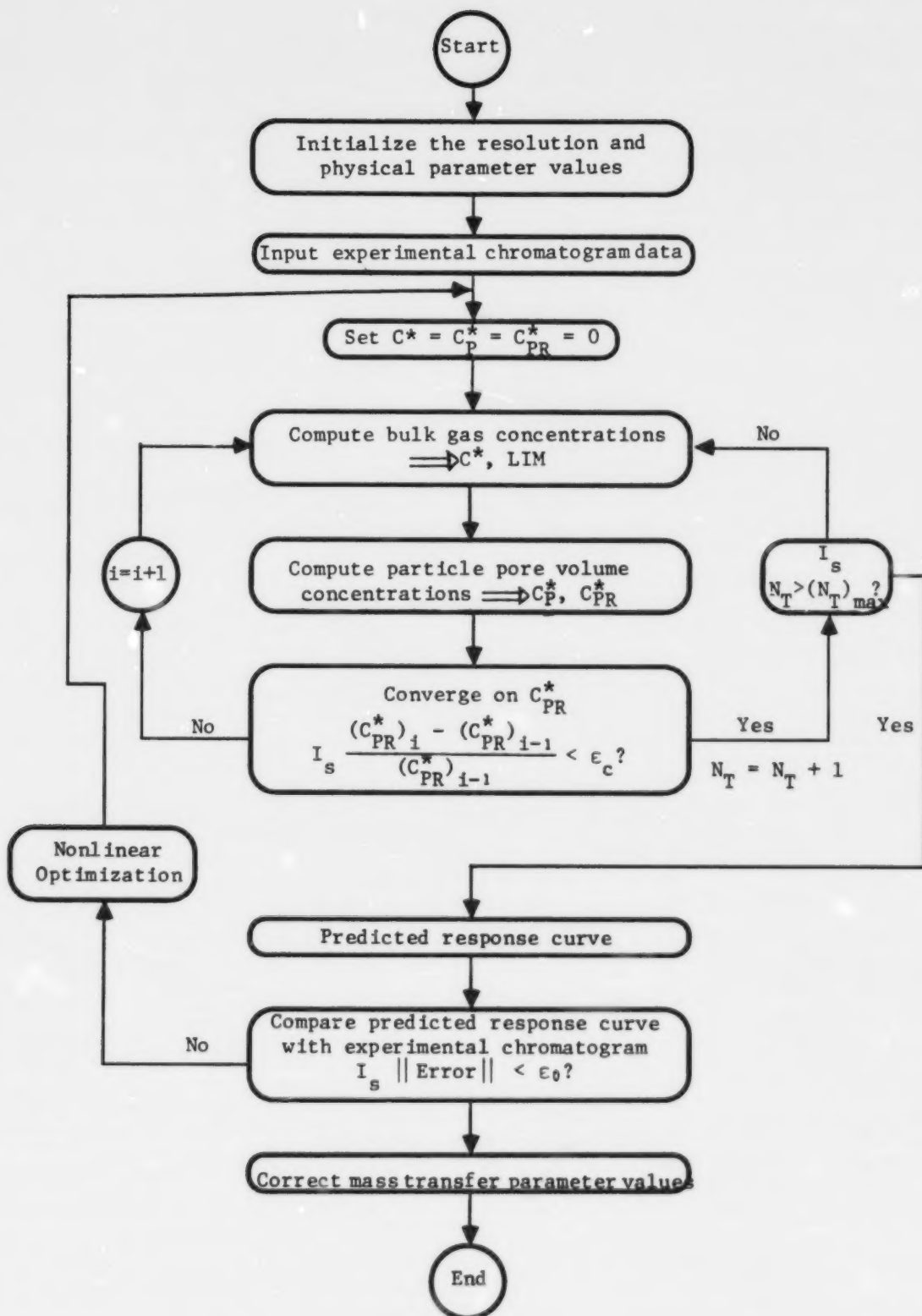


Figure IV.3 - Schematic representation of the parameter estimation algorithm.

denoted by LIM. The concentrations at the particle-bulk gas interface are then computed and denoted by C_R .

If the number of column nodes is large, the determination of the concentration profiles within every particle becomes rather time consuming, so one may choose to calculate every j^{th} particle and interpolate between particles to find the C_R 's. The interpolation can be chosen to be linear or a cubic spline.

If each and every C_R differs by less than a tolerance (TOL) from the previous iteration ($P - 1$), then the concentrations in the bulk gas and at the particle-bulk gas interface are sufficiently converged for the first time step. If, however, C_R has not converged, then the bulk gas mass balance must be recalculated followed by that for the particles until convergence is attained.

Once convergence is achieved, the computation proceeds to the second time step where Gear finite differences are used to represent the accumulation terms. Here again, the calculation is iterative until convergence is attained whence the program can go on to the next time step.

The computation continues until NMAX is reached, at which point the response curve has been obtained. The calculated response curve and the experimental response curves are compared at the selected curve points. An error, or norm, between the curves is calculated according to:

$$\| \text{Error} \| = \left[\sum_{i=1}^m (F_{\text{calc}}(X, t) - F_{\text{obs}}(t))^2 \right]^{1/2} \quad (4.41)$$

where M is the number of curve points. When the norm is less than a specified tolerance (TOLOP), the physical parameter values may be assumed to be correct.

If the norm is greater than TOLOP, then the parameters are optimized using the nonlinear least squares algorithm described in section IV.4 until convergence is achieved or until a maximum specified number of iterations (NOPMAX) is reached.

A program listing is given in Appendix 4.

IV.6 NUMERICAL SIMULATION OF THE CHROMATOGRAPHIC COLUMN BY THE METHOD OF FINITE DIFFERENCES

The developed computer programs were first tested with the chromatographic pulse response data for the nitrogen/activated carbon system given by Wakao and Kaguei [23].

IV.6.1 Nitrogen/activated carbon system

The experimental data for the nitrogen/activated carbon system as given by Wakao and Kaguei [23] are as follows:

Packed bed parameters:

Bed length (L)	: 0.204 m
Bed porosity (ϵ_b)	: 0.380
Particle size (R)	: 1.0×10^{-4} m
Particle porosity (ϵ_p)	: 0.59

Experimental conditions:

Bed temperature (T) : 20°C
 Flow rate : 4.2×10^{-2} m/s

The following parameter estimates as given in reference [23] are used to simulate the chromatographic column with the Kubin-Kucera model:

$$D_{ax} = 4.8 \times 10^{-5} \text{ m}^2/\text{s}$$

$$D_r = 6.3 \times 10^{-7} \text{ m}^2/\text{s}$$

$$K_r = 0.1 \text{ m/s}$$

$$\rho_p K_A = 5.29$$

Initially, the principle resolution parameters such as the time step, the number of nodes (MP) particle and the number of nodes (MB) column were varied to establish their effect on the calculated response signal.

From figure IV.4, it can be seen that as the number of column nodes, MB, is increased, the response curve becomes sharper. The theoretical maximum number of column nodes (defined as the column length divided by the particle diameter) for this example was 102. It can be seen from figure IV.4 MB values greater than the theoretical maximum number ($MB = 102$), the increase in the number of column nodes has an insignificant effect on the shape of the calculated response curve.

Figure IV.5 shows the sensitivity of the response curve to the number of particle nodes (MP) [The response curves are calculated with 102 column nodes]. A variable mesh is used for the particles and the radial discretization of the particles is such that the nodes are more closely

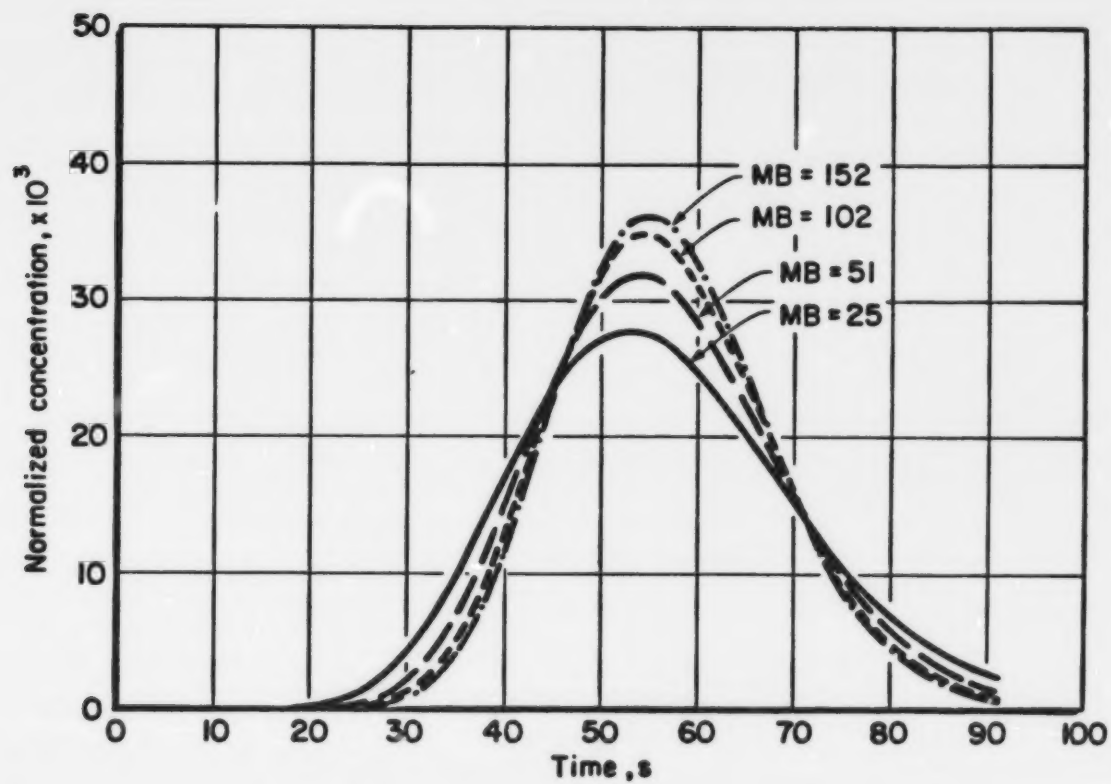


Figure IV.4 - Effect of the number of column nodes (MB) on the calculated response curve.

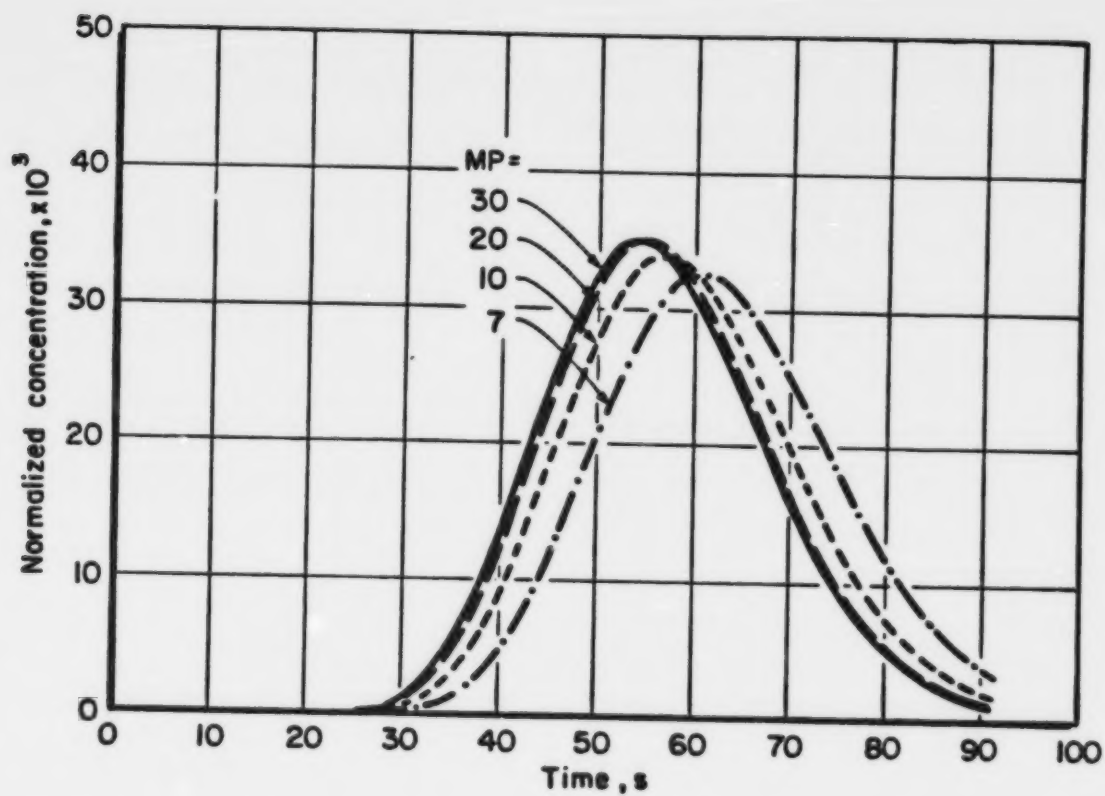


Figure IV.5 - Effect of the number of particle nodes (MP) on the calculated response curve.

spaced in the region close to the particle surface to take into account the sharp concentration gradient. Figure IV.5 shows that at sufficiently high values of particle nodes (for MP 20), the response curve is relatively insensitive to further increase in the number of particle nodes. For this reason 20 particle nodes was assumed to be sufficient to describe the particle fairly accurately.

It was also found that the convergence tolerance criterion (TOL) that can be used to obtain a reasonably accurate description of the response curve depends on the number of particle nodes. With few particle nodes smaller tolerance values were needed thus significantly increasing the amount of computer time. For the case under study, 20 particle nodes (MP = 20) and a tolerance criterion of 0.05 (TOL = 0.05) were found to yield the desired accuracy at the expense of a minimal amount of computer time.

The computed response curve for the test case, calculated with the transport parameters given by Wakao and Kaguei [23] is given in figure IV.6 along with the experimentally obtained response curve. The observed lack of fit may be attributed to errors associated with the values of the transport parameters used. The evolution of the concentration pulse in the bed and the evolution of the concentration profile in the intraparticle void for the first particle are given in figures IV.7 and IV.8 respectively. The figure IV.7 shows clearly the broadening of the concentration pulse as it is propagated along the bed.

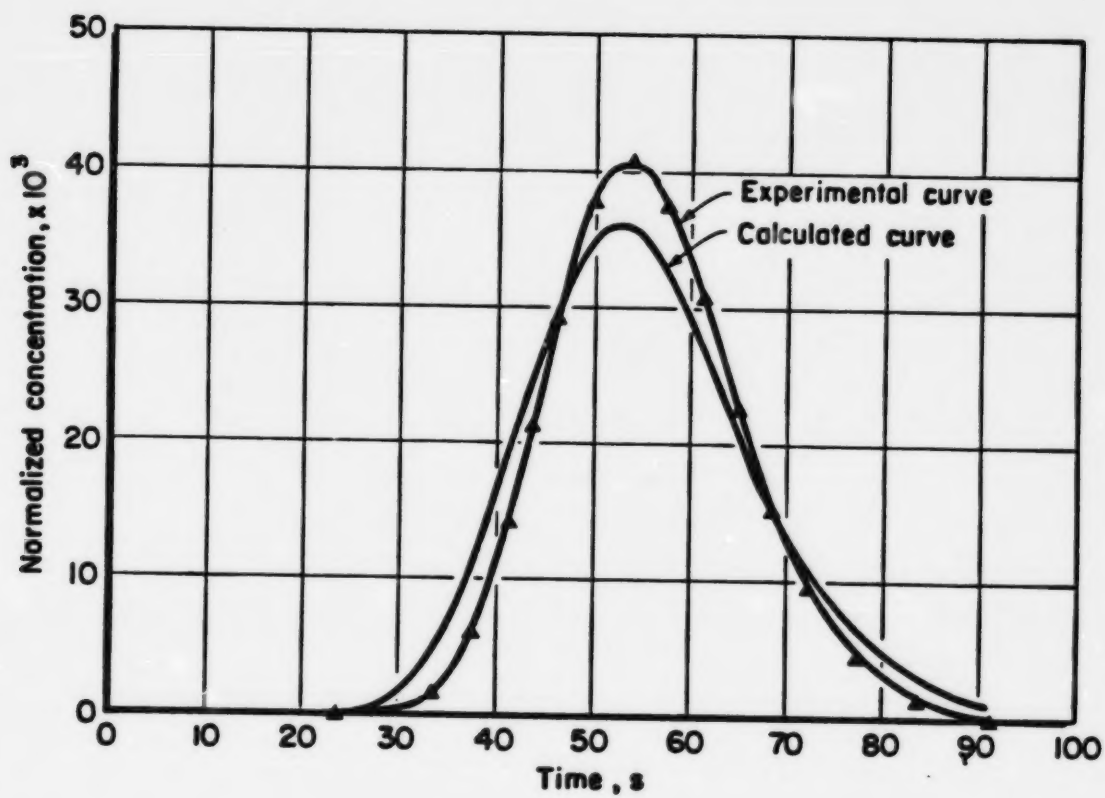


Figure IV.6 - Chromatographic response curves (Nitrogen/Activated carbon).

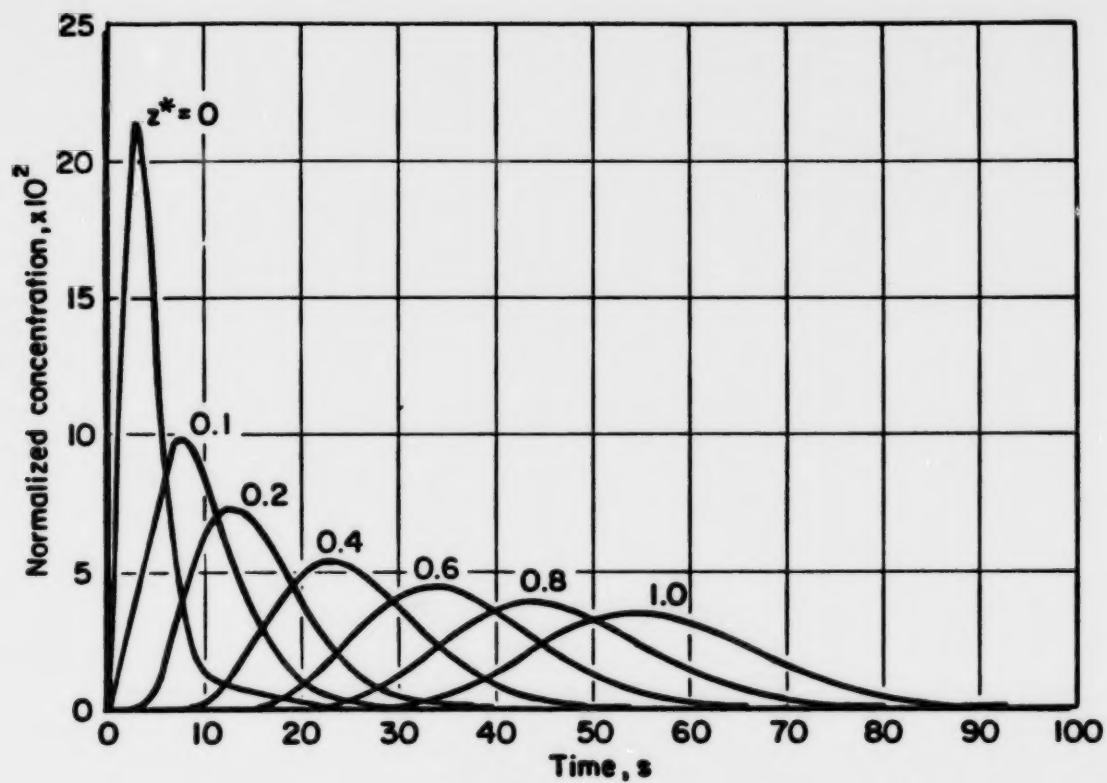


Figure IV.7 - Evolution of the concentration profile of the adsorbate in the bed.

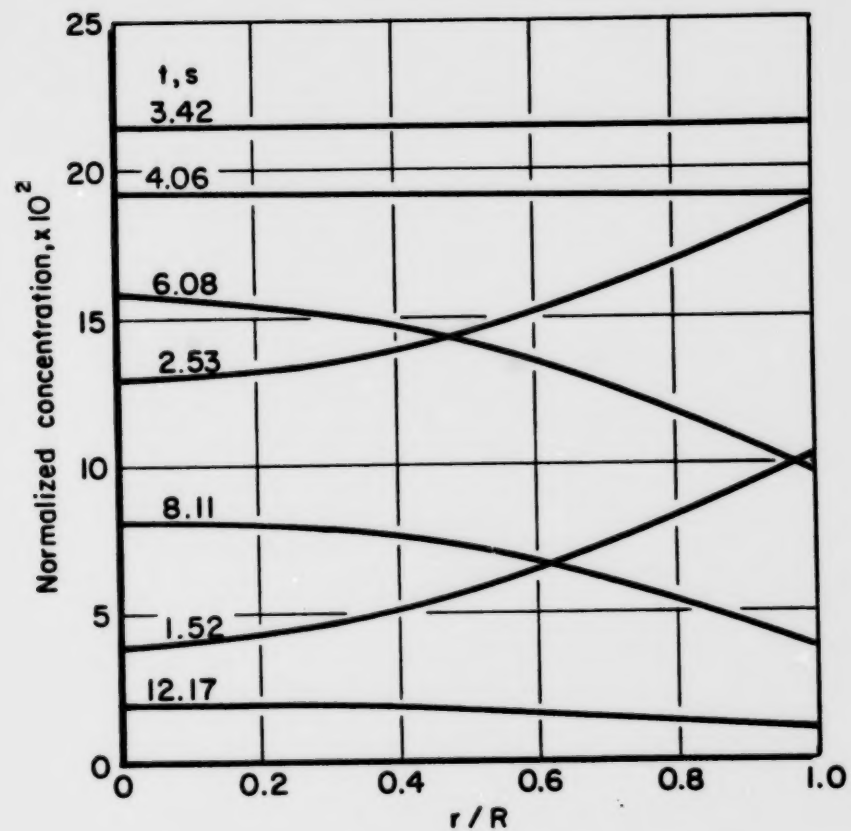


Figure IV.8 - Evolution of the concentration profile of the adsorbate in the particle.

IV.6.1.1 Effect of various transport parameters on the calculated response signal

The effect of variations in the transport parameter values such as D_{ax} (axial dispersion coefficient), D_e (effective intraparticle diffusivity), K_A (adsorption equilibrium coefficient), and K_f (film mass transfer coefficient) was examined by computing the response signals with several different values for each parameter.

Figures IV.9 - IV.13 show the effect of various transport parameters on the calculated response curve. It can be seen immediately that the calculated response curve is significantly sensitive to the parameter values of D_{ax} , D_e and K_A and is least sensitive to the values of K_f . Small changes in the values of K_A have a significant effect on the average retention time and the width of the calculated response signal (fig. IV.12). An increase in the K_A value leads to an increase in both the average retention time and the width of the response signal. From figure IV.13, it can be seen that there is a linear relationship between the average retention time and the adsorption equilibrium constant. The average retention time increases linearly with the adsorption equilibrium constant.

On the other hand, D_{ax} and D_e had little or no effect on the average retention time of the calculated response signal, and even changes in these values as much as by an order of magnitude had only a moderate effect on the width of the calculated signal.

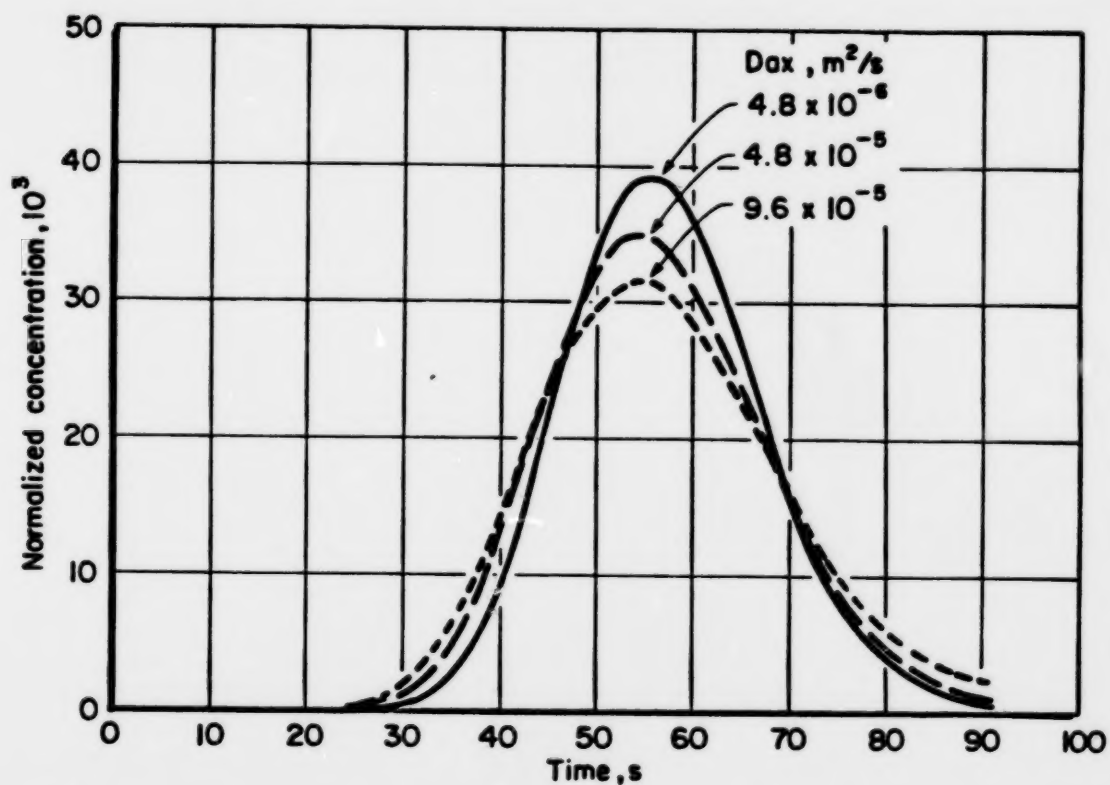


Figure IV.9 - Effect of axial dispersion coefficient (D_{ax}) on the calculated response curve.

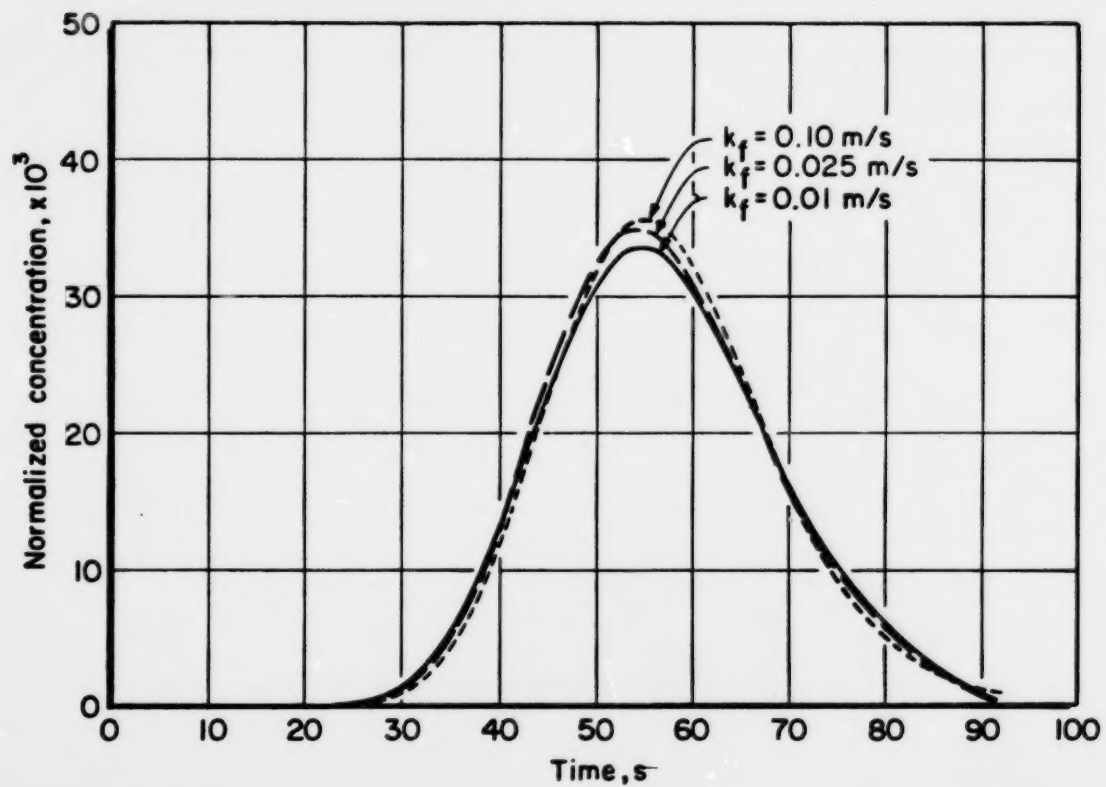


Figure IV.10 - Effect of the fluid to particle film mass transfer coefficient (k_f) on the calculated response curve.

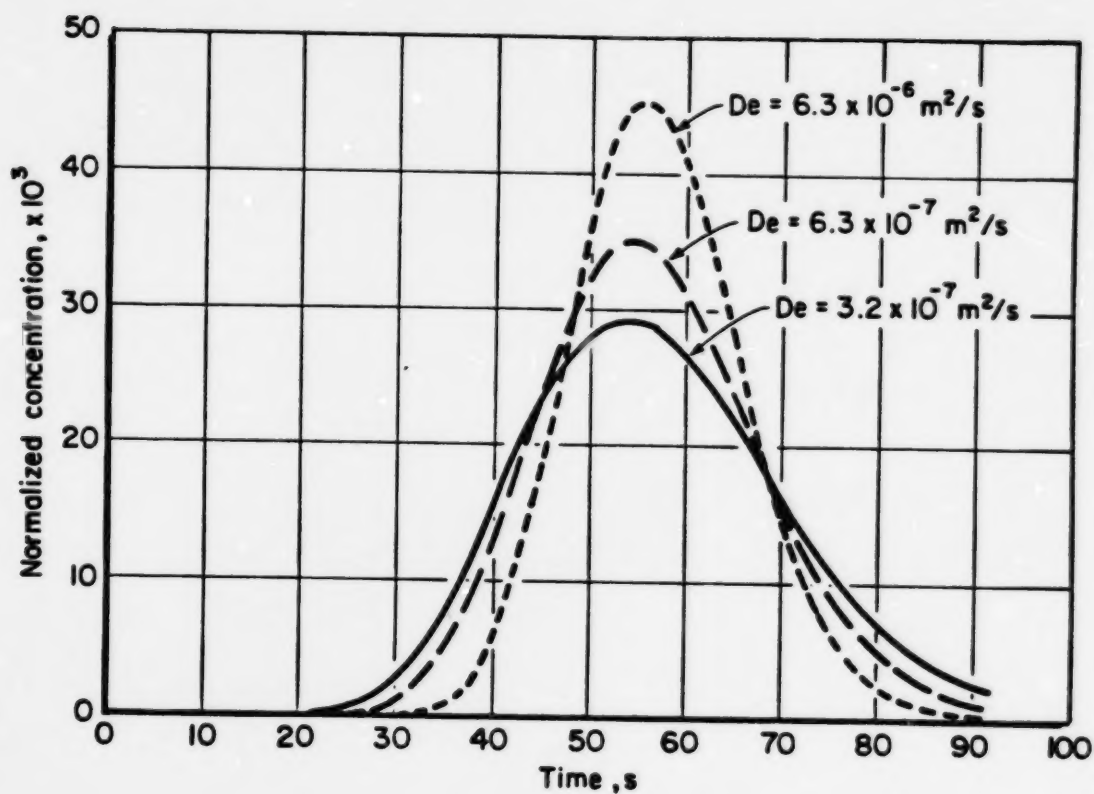


Figure IV.11 - Effect of the effective intraparticle diffusion coefficient (D_e) on the calculated response curve.

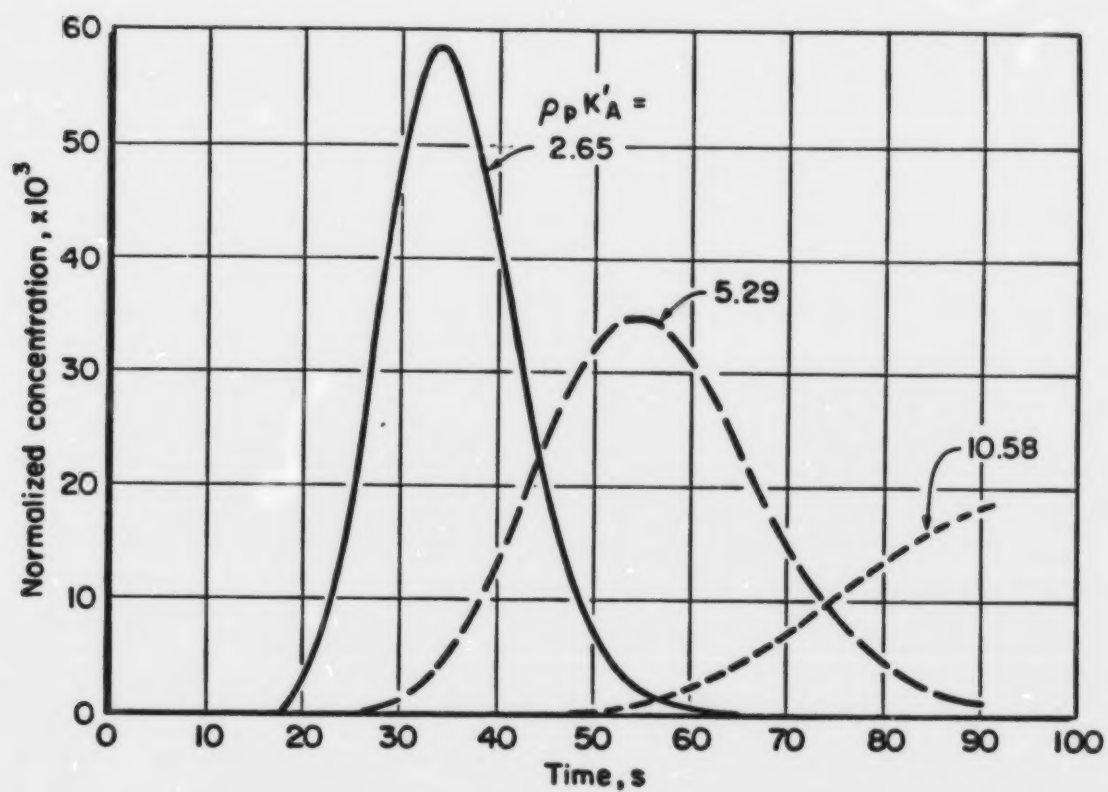


Figure IV.12 - Effect of the adsorption equilibrium constant (K_A) on the calculated response curve.

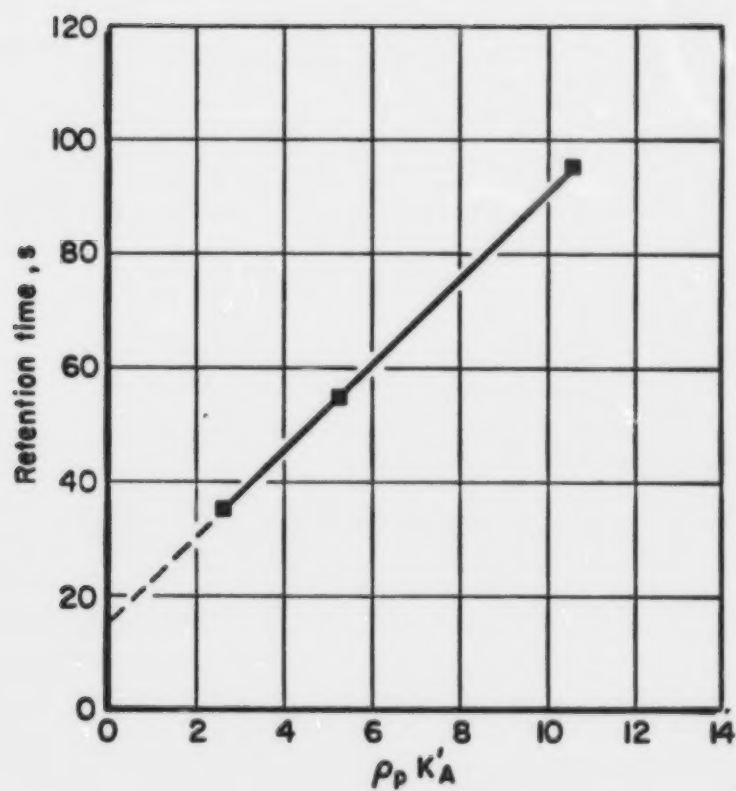


Figure IV.13 - Calculated pulse retention time as a function of the adsorption equilibrium constant.

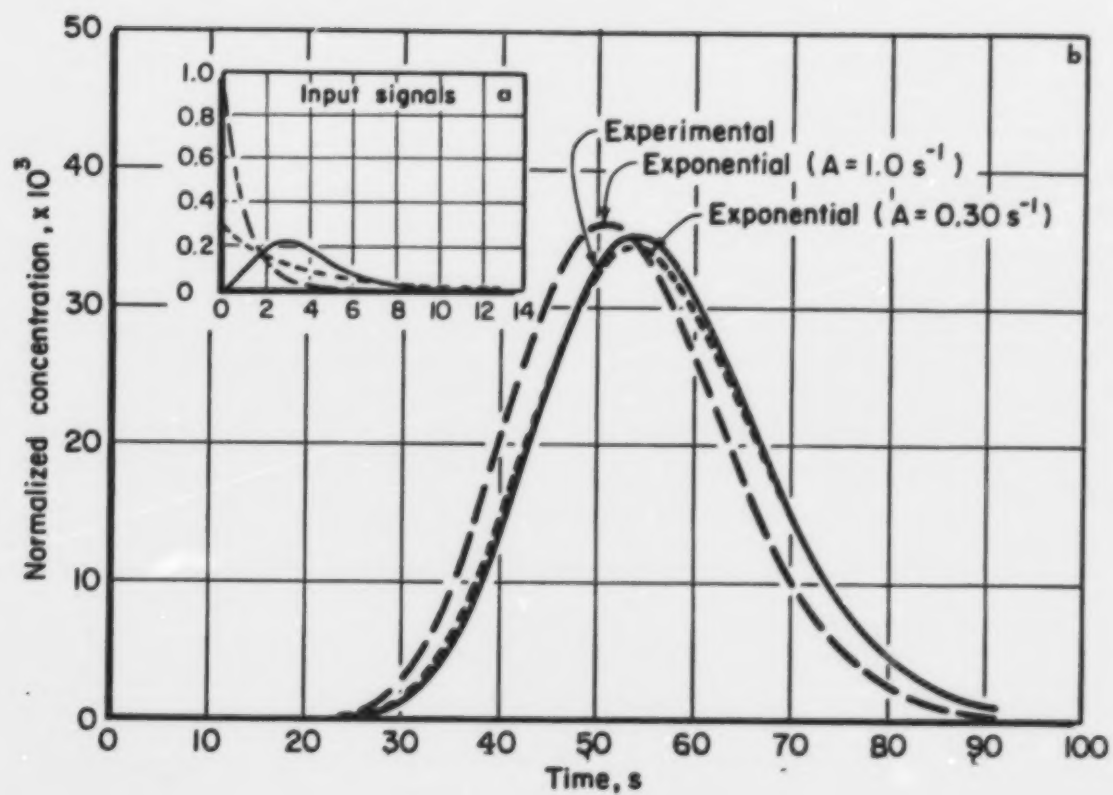


Figure IV.14 - Effect of the input pulse shape on the calculated response curve.

IV.6.1.2 Effect of the input pulse shape on the calculated response signal

More than often the shape of the input concentration pulse to a packed bed is not available. Boniface and Ruthven [41] have shown that an accurate description of the input signal is required to predict accurately the response signal when the retention time is relatively short. They showed that the injection time, defined as the time taken for the inlet concentration to reach $1/e$ of the initial concentration, to be inversely proportional to the carrier gas flow rate. Thus the inlet concentration can be represented as

$$C_1(t) = \frac{1}{a} e^{-at} \quad (4.42)$$

where "a" is chosen such that

$$\int_0^{\infty} C_1(t) dt = 1.0 \quad (4.43)$$

As can be seen from figures IV.14(a) and (b), the form of the input signal is of significant importance. For instance, if the input curve is a rapidly decaying exponential, the response time of the response curve is shortened and the response curve itself is slightly sharpened. If, on the other hand, an exponential input curve roughly approximates the experimental input signal, then the response curves will not differ significantly.

Boniface and Ruthven found for their column that the injection time constant was correlated in terms of the interstitial fluid velocity according to:

$$a = \frac{V \text{ (cm/s)}}{14.0 \text{ cm}} \quad (4.44)$$

For the test example, with $V = 4.20 \text{ cm s}^{-1}$, [the equation (4.44)] is used to find a value for "a". The value of 0.3 found surprisingly coincides with the value of "a" which was used to describe the exponential input signal that yields almost the same response signal as obtained using the experimentally determined input signal.

IV.6.1.3 Optimization of the transport parameters

In the previous example, the calculated response curve with the values of the parameters $D_{ax} = 4.8 \times 10^{-5} \text{ m}^2/\text{s}$, $D_e = 6.3 \times 10^{-7} \text{ m}^2/\text{s}$; $K_f = 0.1 \text{ m/s}$ and $\rho_p K_A = 5.29$ does not fit well with the experimental response curve. For this reason, a tridimensional search in K_A , D_e and D_{ax} was attempted using the above values for the parameters as initial estimates, in order to obtain a better fit; but as found by Wakao [46] previously, a simultaneous determination of D_e and D_{ax} is found to be not feasible. This arises due to the fact that both D_e and D_{ax} influence the shape of the response curve in a similar fashion and this can be clearly seen from figures IV.9 and IV.11.

The method of moments does, however, provide a reliable estimate of the axial dispersion coefficient; so, assuming D_{ax} to be correct, a two dimensional search in $\rho_p K_A$ and D_e was tried. Optimizations were done assuming the theoretical maximum number of column nodes (102), 150 and 200. The converged values of $\rho_p K_A$ and D_e as well as the norm of the residuals are shown in figures IV.15, IV.16 and IV.17 respectively for each optimization.

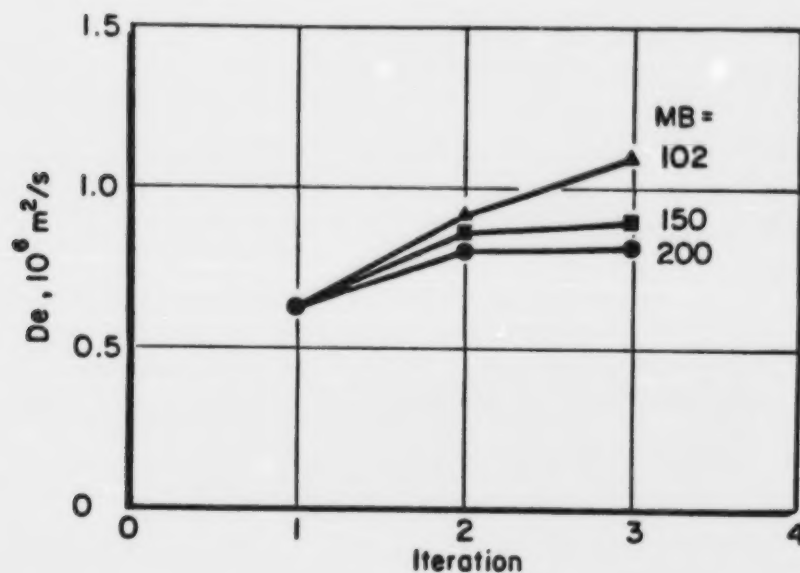


Figure IV.15 - D_e as a function of the optimization iterations for various values of MB.

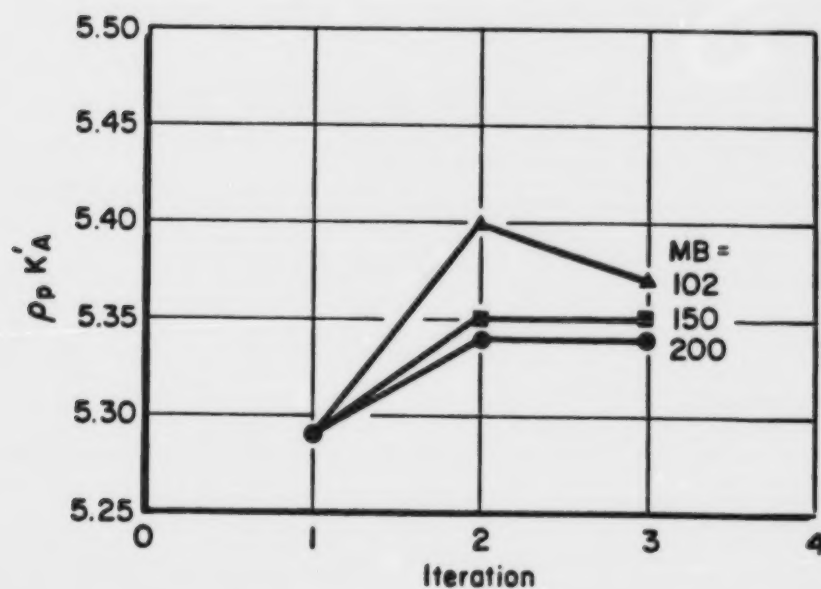


Figure IV.16 - $\rho_p K_A$ as a function of the optimization iterations for various values of MB.

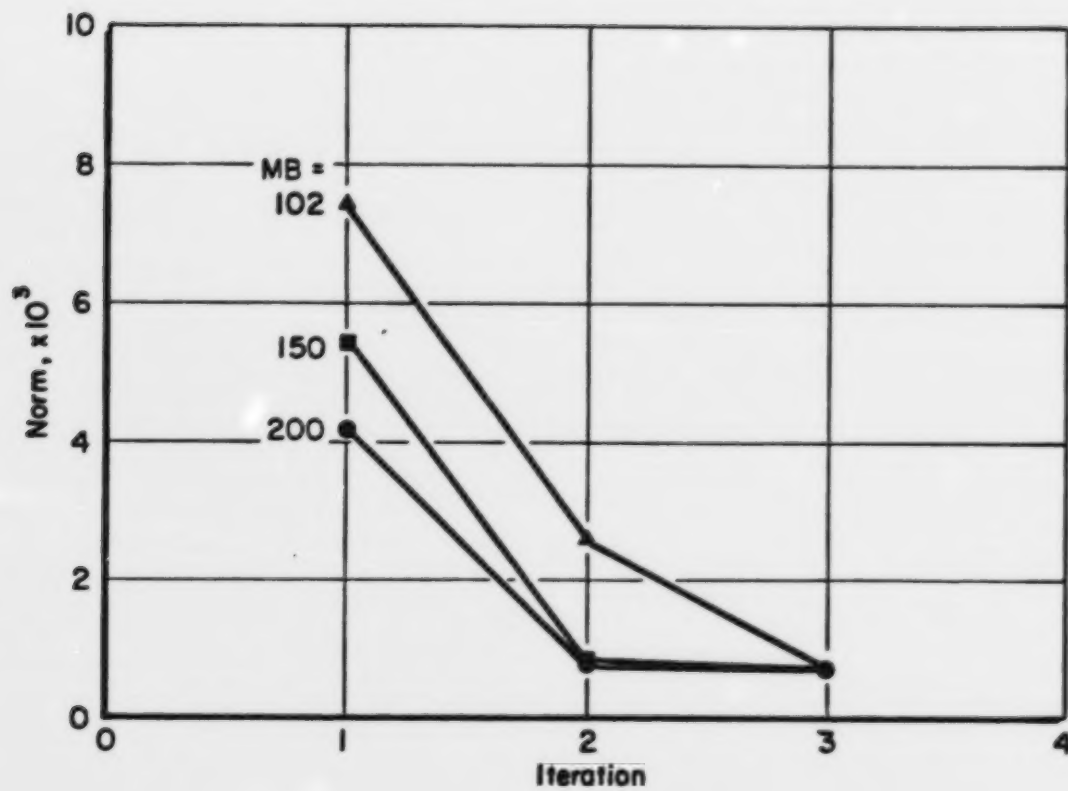


Figure IV.17 - Norm as a function of the optimization iterations for various values of MB.

In each case, the response curves were fitted at five curve points: two before the peak maximum, one at the peak maximum and two after the peak maximum. Figure IV.17 shows that in all three cases the optimizations converged in three iterations. The rapid convergence was obtained since the Jacobian matrix was determined by numerical differences until the norm was less than 0.007, where Broyden updating was found to be sufficiently accurate. Except for the optimization with MB = 102, Broyden updating could be used for the third iteration. It is found that increasing the number of column nodes tended to reduce the deviation between the initial values of D_e and $\rho_p K_A$ given by Wakao and caused an improvement in the convergence.

The 2-D optimization with 102 column nodes is shown in figure IV.18. The calculated response curve using the values of D_e , $\rho_p K_A$ and D_{s1} given by Wakao is shown with the experimental curve and the curve after optimization. It can be seen that the calculated response curve after optimization fits almost perfectly the experimental one with a norm of 0.0007 for 5 curve points used.

Table IV.3 - Optimized parameter values.

Parameter	Literature value	Optimized value
$\rho_p K_A$	5.29	5.37
D_e (m^2/s)	0.63×10^{-6}	1.01×10^{-6}

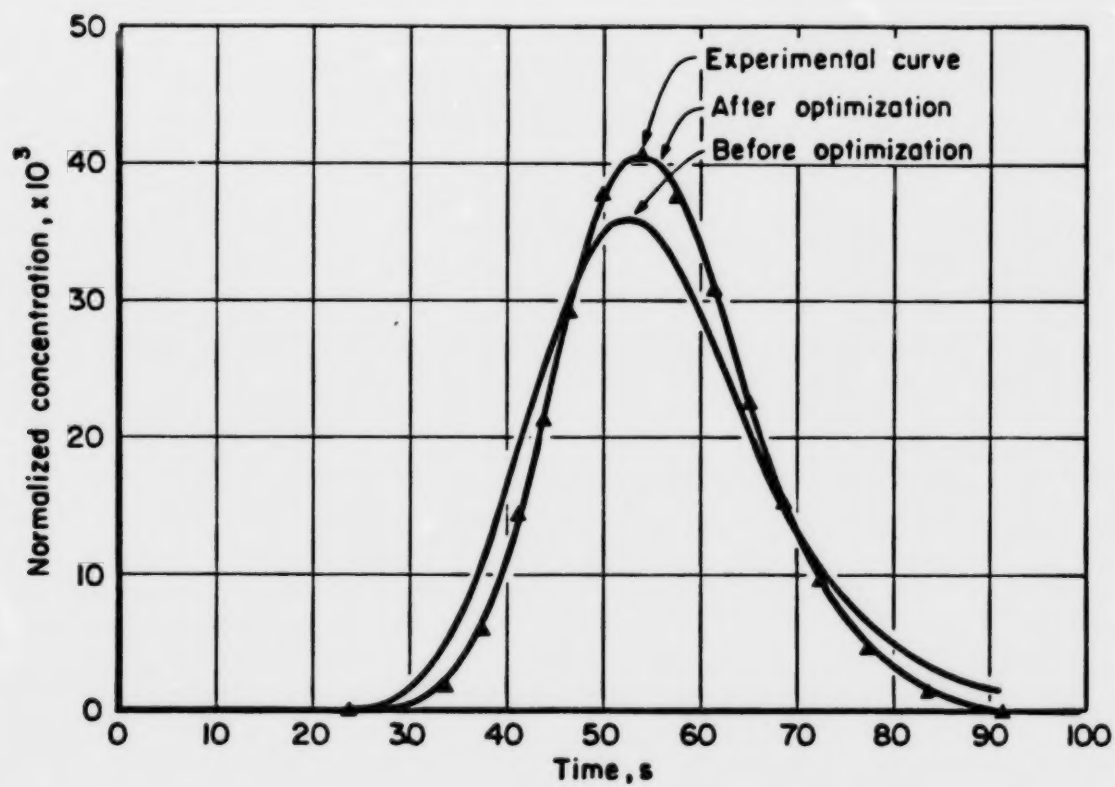


Figure IV.18 - Chromatographic response curves (Nitrogen/Activated carbon).

IV.6.2 Nitrogen/H-mordenite

The H-mordenite zeolite particles used, have a bidispersed porous structure and preferably, the mathematical model describing the dynamics of the adsorption column should take into account this bidispersed nature of the pore structure of the particles. The Kubin-Kucera adsorption model may, however, still be used to evaluate an intraparticle effective diffusivity coefficient which is representative of the combined macropore-micropore diffusion process.

Initially, the Kubin-Kucera adsorption model was used in attempt to predict the response curve for adsorption of nitrogen on H-mordenite. The initial estimates of the physical parameters were determined using the method of moments as described in section IV.2. [Relevant computer programs are found in Appendix 3].

IV.6.2.1 Parameter estimation by the moment method

System	: Nitrogen/H-mordenite
Packed bed length (L)	: 0.329 m
Bed void fraction (ϵ_b)	: 0.40
Average particle radius (R)	: 3.0×10^{-4} m
Intraparticle void fraction (ϵ_p)	: 0.6
Bed temperature (T)	: 125°C
Flow rates (cm/s)	: 3.36; 6.02; 9.03

The experimental chromatograms were first digitized for each experiment. The method used and the relevant computer programs are given in Appendix 3. The experimental moments were calculated from the digitized

curves and required moment plots are given in figures IV.19 and IV.20. From these plots the transport parameters were determined according to the method described in section IV.2.

The moment method estimates of the transport parameters and other important parameters estimated from various correlations are given in table IV.4.

Table IV.4 - Estimates of various transport parameters.

Parameter	Estimated value
K_f (m/s)	1.51×10^{-1}
$\rho_p K_A$	1.16
D_e (m ² /s)	1.32×10^{-7}
D_{ax} (m ² /s)	1.91×10^{-5}

IV.6.2.2 Results from numerical simulations and parameter optimization runs

The chromatographic column for the nitrogen/H-mordenite system was simulated numerically using the method of finite differences. The column was simulated using the input pulse data for the run conducted with an interstitial gas velocity of 6.02 cm/s ($N_{Re} = 0.113$) and the transport parameter values estimated from the moment method.

The response signal was calculated using similar column and parti-

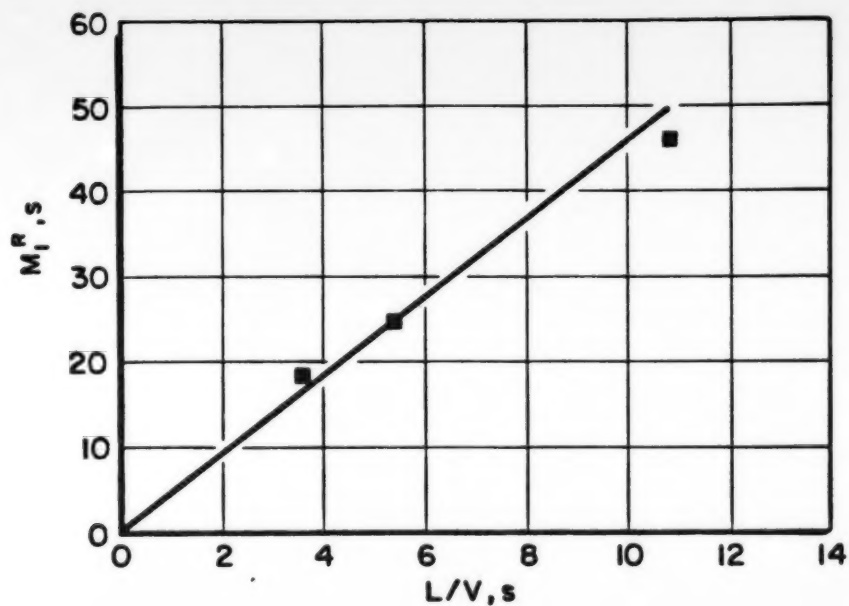


Figure IV.19 - First moments plot for the Nitrogen/H-mordenite system.

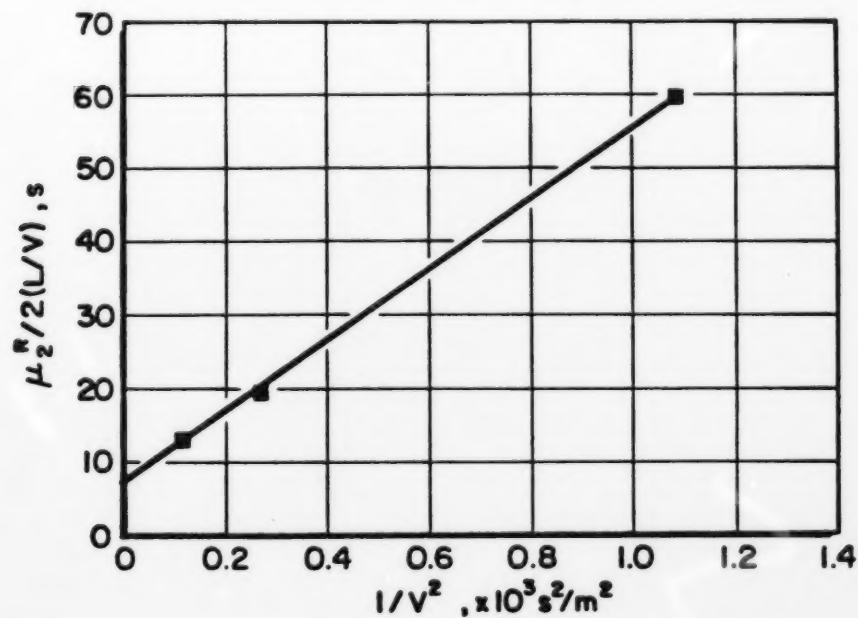


Figure IV.20 - Second central moments plot for the Nitrogen/H-mordenite system.

cle discretization parameter values ($MB = 102, 250$; $MP = 20$) as used for the previous test case. A time step size of 0.0044 s was found to be appropriate for the given case. The calculated response curves for MB (number of column nodes) values of 102 and 250 are given in figure IV.20 along with the experimental response signal.

As can be seen in figure IV.20 the average retention time (time measured at the peak maximum) is well predicted although the overall fit of the calculated response curve with that of the experimental response curve is poor.

This lack of fit can arise if the parameter values predicted by the method of moments such as the effective diffusivity or the axial dispersion coefficient are poor estimates or that the number of column nodes is simply too small. Since, the method of moments does provide an accurate estimate of the axial dispersion coefficient, a two dimensional optimization of the effective diffusivity and the equilibrium constant was attempted. The effective diffusivity was increased by many orders of magnitude in order to correct the deviation, which of course is incorrect and meaningless.

The response curve sensitivity to the number of column nodes was investigated by increasing the number to 250 . As depicted in figure IV.21, many more column nodes than this would be required to full close the gap between the response curves. The theoretical maximum number of nodes for this column is, however, 1150 which is much larger than that of Wakao's column (102). So, probably 1150 column nodes would provide a much better representation of the response curve.

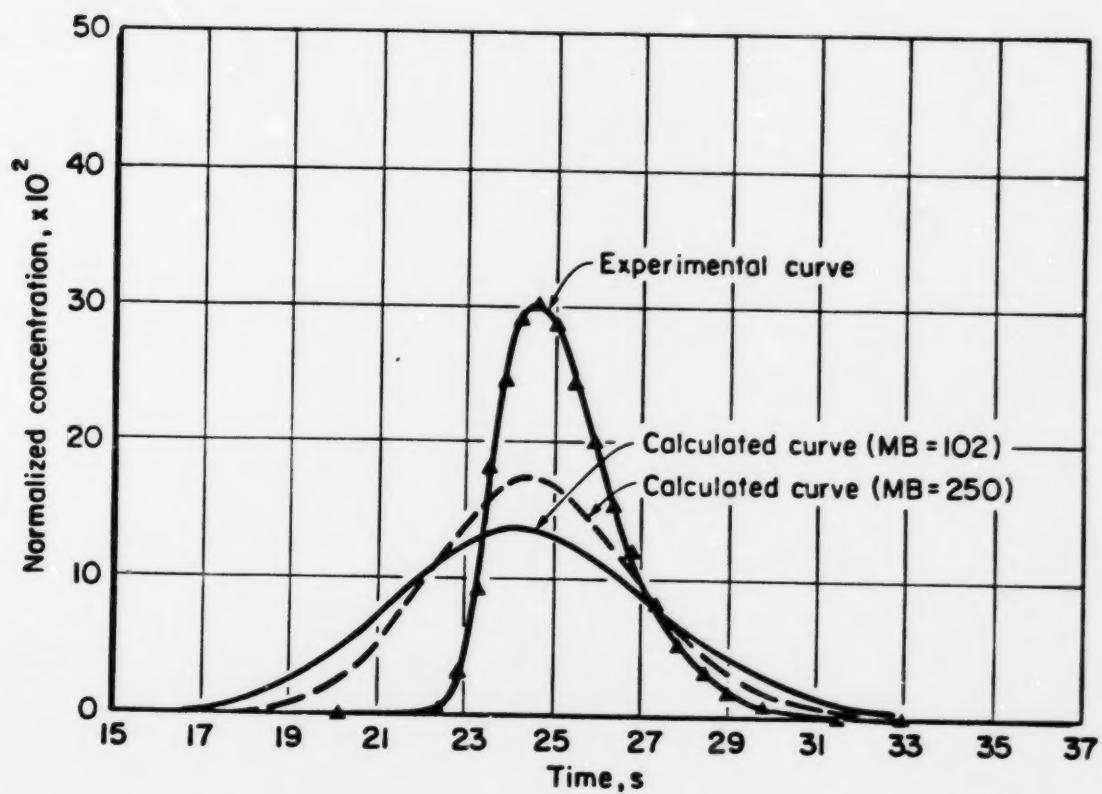


Figure IV.21 - Chromatographic response curves (Nitrogen/H-mordenite system).

The problem is that the computation time for a column having 1150 nodes becomes prohibitively large unless high speed computers are available for such problems. A possible improvement, however, could be to use the method of successive over-relaxation (SOR) for solving the huge matrix systems [38].

V. CONCLUSION

Chromatographic pulse response data were obtained with several nitrogen compounds/zeolite systems. A general characteristic of these systems is their nonlinear behaviour. As a result, the chromatographic pulse response data obtained of these system cannot be analysed using the conventional analysis techniques applicable only to linear systems (section I.7).

In the present work, a parameter estimation technique is developed that can be applied to both linear and nonlinear models. The developed numerical method uses finite differences to solve the model equations, which is coupled to a nonlinear least square routine for optimization of transport parameters.

The computer programs developed were tested using chromatographic pulse response data given in the literature [23] for nitrogen/activated carbon system. The column dynamics was described using the Kubin-Kucera model (p. 161) with a linear adsorption isotherm. To successfully determine the parameters involved in the model, axial dispersion coefficient (D_{ax}) needed to be determined by an independant technique. The values of K_A and D_e are then easily found by a two dimensional search.

The search algorithm based on nonlinear least squares with QR factorization of the Jacobian performed well in fitting the calculated response curve to the experimental chromatogram by adjusting K_A and D_e . The algorithm which a Gauss-Newton type converged in as few as 3 iterations when good initial estimates of the transport parameter values are available.

The optimized transport parameter values were found to be in excellent agreement with those given in the literature.

Application of the developed method to the nitrogen/H-mordenite system did not meet with the same success. The initial poor performance of the method is caused by the poor choice of several parameters such as the time step (Δt), number of column nodes (MB) and the number of particle nodes (MP) for this system. The successful performance of the method depends on the appropriate choice of these parameters.

Although, the developed method was tested with a linear model, the computer programs can be easily modified to treat nonlinear models and also to take into account the bidispersed pore structure of commonly used zeolite adsorbent.

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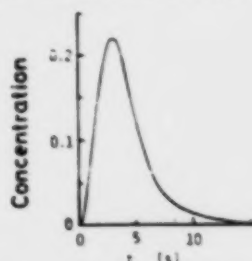
APPENDIX 1

Digitization of analog signals

Digitization program:

A digitization program adapted to the IBM personal computer and the Hewlett-Packard 7475A plotter equipped with a cross-hair digitizing device was available. (See programme de numérisation, appendix 1).

To investigate the precision of the digitization process, the input curve from Wakao and Kaguei's example shown below (actual size) was digitized thrice and was compared with the actual experimental values for three curve points. The results are summarized below:



Accuracy of digitization

(average of 3)

Time	Actual conc.	Digitized conc.
0.85	0.0521	0.0564 ± 0.0073
2.97	0.2164	0.2157 ± 0.0012
7.86	0.0300	0.0307 ± 0.0009

The digitized concentrations were found to be very close to the actual concentrations for all three curve points and are certainly within

the given standard deviations. Upon observing the relative values of the standard deviations, one can see that the error in digitization becomes large where the chromatographic curve is steepest. For instance, at the first curve point ($t = 0.85$ s) where the curve is steepest, the standard deviation is large; whereas, at the curve peak and after it flattens (at $t = 2.97$ s and $t = 7.86$ s), the standard deviation is much less.

```

0040 INPUT E1
0050 RETURN
0060 CLS:LOCATE 2,5:PRINT "ENTRE LA VALEUR MAX. DE L'ECHELLE EN X"
0070 INPUT GX
0080 LOCATE 4,5:PRINT "ENTRE LA VALEUR MIN. DE L'ECHELLE EN X"
0090 INPUT PX
0100 RETURN
0110 LOCATE 8,5:PRINT "ENTRE LE NOMBRE D'INTERVALLES COMPLET SUR L'AXE DES Y"
0120 INPUT C2
0130 LOCATE 10,5:PRINT "ENTRE LA PUISSANCE EN Y A L'ORIGINE"
0140 INPUT E2
0150 RETURN
0160 LOCATE 8,5:PRINT "ENTRE LA VALEUR MAX. DE L'ECHELLE EN Y"
0170 INPUT GY
0180 LOCATE 10,5:PRINT "ENTRE LA VALEUR MIN. DE L'ECHELLE EN Y"
0190 INPUT PY
0200 RETURN
0210 X(I)=10^(((A-B1)*COS(TET)+(B-B2)*SIN(TET))/D1+E1)
0220 RETURN
0230 X(I)=((A-B1)*COS(TET)+(B-B2)*SIN(TET))/DNX*(GX-PX)+PX
0240 RETURN
0250 X(I)=10^(((B-B2)*SIN(PHI)+(A-B1)*COS(PHI))/D2+E1)
0260 RETURN
0270 X(I)=((A-B1)*COS(PHI)+(B-B2)*SIN(PHI))/DNY*(GX-PX)+PX
0280 RETURN
0290 Y(I)=10^(((B-B2)*SIN(PHI)+(A-B1)*COS(PHI))/D2+E2)
0300 RETURN
0310 Y(I)=((B-B2)*SIN(PHI)+(A-B1)*COS(PHI))/DNY*(GY-PY)+PY
0320 RETURN
0330 Y(I)=10^(((ID1-A)*COS(TET)-(B-ID2)*SIN(TET))/D1+E2)
0340 RETURN
0350 Y(I)=((ID1-A)*COS(TET)-(B-ID2)*SIN(TET))/DNX*(GY-PY)+PY
0360 RETURN
0000 REM ***** INITIALISATION *****
0010 DIM CH$(25)
0020 T1=T2=0
0030 DIM X(50),Y(50)
0040 C1=C2=1
0050 B1=B2=0
0060 REM *****
0070 REM *          SOUS ROUTINE DE TEXTE          *
0080 REM *****
0090 CH$(1)="F1 LOG-LOG TYPE 1"
0100 CH$(2)="F2 LINEAIRE-LINEAIRE TYPE 1"
0110 CH$(3)="F3 LINEAIRE-LOG TYPE 1"
0120 CH$(4)="F4 LOG-LINEAIRE TYPE 1"
0130 CH$(5)="F5 LOG-LOG TYPE 2"
0140 CH$(6)="F6 LINEAIRE-LINEAIRE TYPE 2"
0150 CH$(7)="F7 LINEAIRE-LOG TYPE 2"
0160 CH$(8)="F8 LOG-LINEAIRE TYPE 2"
0170 CH$(9)="F1 NUMERISE UNE PREMIERE COURBE"
0180 CH$(10)="F2 NUMERISE AUTRE COURBE DU MEME GRAPHE"
0190 CH$(11)="F3 IMPRIMER "
0200 CH$(12)="F4 ENREGISTRER"
0210 CH$(13)="F5 RECUPERER"
0220 CH$(14)="F6 TERMINER"
0230 RETURN

```

```

4200 CLOSE #1
4210 CLS:PRINT TAB(10)"VOICI LES DONNEES DU FICHIER:":PRINT ""
4220 PRINT TAB(20)TI$:PRINT ""
4230 GOSUB 1420
4250 RETURN
5000 REM *****
5010 REM *          FIN DU PROGRAMME          *
5020 REM *****
5030 CLS:PRINT "PROGRAMME TERMINE"
5040 KEY ON
5050 END
6000 REM *****
6010 REM *          SOUS ROUTINE DE COMMANDE AU PLOTTER          *
6020 REM *****
6030 PRINT #1,"DF:"
6040 PRINT #1,"OS:"
6050 INPUT #1,S
6060 S=INT(S/4)
6070 IF S=INT(S/2)*2 THEN 6040
6080 PRINT #1,"OD:"
6090 RETURN
6100 REM ***** TRI DES X CROISSANT *****
6110 FOR J=3 TO (I-1)
6120 IF X(J)>X(J-1) THEN 6190
6130 FOR K=J TO 3 STEP -1
6140 IF X(K)>X(K-1) THEN 6180
6150 BIDX=X(K-1):BIDY=Y(K-1)
6160 X(K-1)=X(K):Y(K-1)=Y(K)
6170 X(K)=BIDX:Y(K)=BIDY
6180 NEXT K
6190 NEXT J
6200 RETURN
6300 REM ***** IMPRESSION DE TEXTE *****
6310 LOCATE 8,3:PRINT "PLACER L'ORIGINE DE VOTRE GRAPHE AU COIN INFERIEUR DROIT
DU PLOTTER"
6320 RETURN
6330 LOCATE 8,3:PRINT "PLACER L'ORIGINE DE VOTRE GRAPHE AU COIN INFERIEUR GAUCHE
DU PLOTTER"
6340 RETURN
7000 REM ***** PRECAUTIONS AVEC AXES LOG *****
7010 LOCATE 12,26:PRINT "*** ATTENTION ***"
7020 LOCATE 13,3:PRINT "SI VOS AXES LOG NE SE TERMINENT PAS PAR UN CYCLE COMPLET
PLACER VOTRE PLUME"
7025 LOCATE 14,3:PRINT " COMME SUIV:"
7030 LOCATE 15,3:PRINT "-VOUS DEVEZ POSITIONNER SUR LA FIN DU DERNIER CYCLE COMPLET
COMME AU 'o'"
7035 LOCATE 16,3:PRINT "CI DESSOUS (CAS log-log AUCUN COMPLET) : return pour con
tinuer"
7040 LINE (80,140)-(200,180),,B
7050 LINE (300,140)-(420,180),,B
7060 LOCATE 19,10:PRINT "Y"
7070 LOCATE 24,25:PRINT "X"
7080 LOCATE 18,24:PRINT "o":LOCATE 22,11:PRINT "o":LOCATE 22,24:PRINT "o"
7090 LOCATE 23,39:PRINT "Y"
7100 LOCATE 19,54:PRINT "X"
7110 LOCATE 18,53:PRINT "o":LOCATE 22,40:PRINT "o":LOCATE 22,53:PRINT "o"
7120 REP#=INKEY$: IF REP#<>"" THEN RETURN
7130 GOTO 7120
7200 REM ***** TEST DE FIN DE LECTURE *****
7210 LOCATE 13,3:PRINT "return POUR CONTINUER"
7220 RET#=INKEY$: IF RET#<>"" THEN RETURN
7230 GOTO 7220
8000 REM ***** LECTURE DES COORDONNEES DES AXES *****
8010 CLS:LOCATE 2,5:PRINT "ENTRE LE NOMBRE D'INTERVALLES COMPLET SUR L'AXE DES
X"
8020 INPUT C1

```

```

1455 PRINT "":PRINT "      return pour retour au menu"
1460 CLOSE #1
1465 REP2$=INKEY$:IF REP2$<>" " THEN RETURN
1470 GOTO 1465
1490 RETURN
1000 REM *****
1010 REM *          SORTIES SUR IMPRIMANTE          *
2020 REM *****
2030 CLS:PRINT "L'IMPRIMANTE PRETE ?"
2040 PRINT "":PRINT "APPUI UNE TOUCHE SI OUI"
2050 RET$=INKEY$:IF RET$<>" " THEN 2070
2060 GOTO 2050
2070 LPRINT TAB(20) TI$:LPRINT ""
2080 LPRINT TAB(20)"COURBE: ", CO$:LPRINT TAB(8)"-----"
2090 LPRINT TAB(10) AB$ TAB(30) Z$:LPRINT TAB(8)"-----"
2100 FOR J=2 TO I-1
2110 LPRINT TAB(10) X(J) TAB(30) Y(J)
2120 NEXT J
2130 LPRINT TAB(8)"-----":LPRINT"":LPRINT ""
2140 CLOSE #1
2150 RETURN
3000 REM *****
3010 REM *          ENREGISTRE SUR DISQUETTE          *
3020 REM *****
3030 CLS:LOCATE 5,5:PRINT "ENTRE LE NOM DE VOTRE FICHIER"
3040 LOCATE 7,5:PRINT "IL DOIT AVOIR LA FORME: 'AB12BBW3.DAT'"
3050 INPUT NOM$
3060 LOCATE 9,7:PRINT "SUR DISQUE  A   OU   B  "
3070 INPUT DIS$
3080 NOMF$=DIS$+"": "+NOM$
3090 OPEN "o",1,NOMF$
3100 PRINT #1,I
3110 PRINT #1,TI$
3120 PRINT #1,CO$
3130 PRINT #1,Z$
3140 PRINT #1,AB$
3150 FOR J=2 TO I
3160 PRINT #1,Y(J)
3170 NEXT
3180 FOR J=2 TO I
3190 PRINT #1,X(J)
3200 NEXT
3210 CLOSE #1
3220 RETURN
4000 REM *****
4010 REM *          RECUPERE DES DONNEES DANS LE FICHIER          *
4020 REM *****
4030 CLS:PRINT "ENTRE LE NOM DU FICHIER "
4040 INPUT NOM$
4050 LOCATE 4,2:PRINT "DISQUE  A   OU   B  "
4060 INPUT DIS$
4070 NOMF$=DIS$+"": "+NOM$
4080 OPEN "i",1,NOMF$
4090 INPUT #1,I
4100 INPUT #1,TI$
4110 INPUT #1,CO$
4120 INPUT #1,Z$
4130 INPUT #1,AB$
4140 FOR J=2 TO I
4150 INPUT #1,Y(J)
4160 NEXT
4170 FOR J=2 TO I
4180 INPUT #1,X(J)
4190 NEXT

```

```

835 LOCATE 4,3:PRINT "INTRODUIRE LA PLUME A FIBRE OPTIQUE A LA MAIN SUR LE CHARI
OT"
845 LOCATE 6,3:PRINT "PLACER VOTRE FEUILLE SUR LE PLOTTER COMME SUIT : "
850 IF QQ>4 THEN GOSUB 6300
855 IF QQ<5 THEN GOSUB 6330
860 LOCATE 10,3:PRINT "A L'AIDE DU CLAVIER DU PLOTTER: PLACER LA POINTE DE LA FL
UME "
865 LOCATE 11,3:PRINT "AU COIN SUPERIEUR DROIT DU GRAPHE"
870 IF QQ<2 AND QQ<6 THEN GOSUB 7000
875 IF QQ=2 OR QQ=6 THEN GOSUB 7200
880 CLS:SCREEN 0,0:PRINT "LORSQUE BIEN POSITIONNE APPUYE SUR LA TOUCHE enter du
PLOTTER"
890 OPEN "COM1:9600,S,7,1,RS,CS65535,DS,CD" AS #1
920 GOSUB 6000
930 INPUT #1,T1,T2,P
935 LOCATE 3,2:PRINT "PLACER LA PLUME AU COIN INFERIEUR DROIT DU GRAPHE"
937 GOSUB 6000:INPUT #1,ID1,ID2,P
940 LOCATE 6,2:PRINT "PLACER LA PLUME SUR LE COIN INFERIEUR GAUCHE"
970 GOSUB 6000
980 INPUT #1,B1,B2,P
990 ON QQ GOSUB 8000,8060,8060,8000,8000,8060,8060,8000
1000 ON QQ GOSUB 8110,8160,8110,8160,8110,8160,8110,8160
1001 CLS:LOCATE 5,2:PRINT "CORRECTION DES COORDONNEES ? (O/N)"
1002 INPUT B#
1003 IF B#="O" THEN GOTO 990
1005 CLOSE #1
1010 IF QQ>4 THEN BID=C2:C2=C1:C1=BID
1100 REM *****
1110 REM *          LECTURE DES POINTS D'UNE COURBE          *
1120 REM *****
1130 CLS:PRINT "          LECTURE DES POINTS DE LA COURBES"
1140 LOCATE 3,1:PRINT "INSTRUCTIONS:"
1150 LOCATE 5,8:PRINT "-POUR CHAQUES POINTS PLACE LA PLUME CORRECTEMENT ET TAPE
enter SUR LE PLOTTER"
1160 LOCATE 8,1:PRINT "-POUR LA FIN DES LECTURES D'UNE COURBE RETAPER enter SUR
PLOTTER"
1162 LOCATE 12,5:PRINT "appui une touche pour fin des instructions"
1164 RET#=INKEY#:IF RET#<>"" THEN 1170
1166 GOTO 1164
1170 DNX=SQR((ID1-B1)^2+(ID2-B2)^2)
1172 DNY=SQR((T2-ID2)^2+(T1-ID1)^2)
1174 TET=ATN((ID2-B2)/(ID1-B1))
1176 PHI=TET+3.141593/2
1178 D1=DNX/C1:D2=DNY/C2
1200 I=2
210 CLS:LOCATE 14,5:PRINT "ENTRE LE NOM DE LA COURBE"
220 LOCATE 15,5:INPUT CO#
1230 FOR J=1 TO 50
1240 X(J)=0:Y(J)=0
250 NEXT J
1260 OPEN "COM1:9600,S,7,1,RS,CS65535,DS,CD" AS #1
1270 LOCATE 17,2:PRINT "POINT NO: ",(I-1)
280 GOSUB 6000
1290 INPUT #1,A,B,P
1300 ON QQ GOSUB 8210,8230,8230,8210,8250,8270,8270,8250
1310 ON QQ GOSUB 8290,8310,8290,8310,8330,8350,8330,8350
1320 IF (X(I)=X(I-1)) AND (Y(I)=Y(I-1)) THEN 1350
1330 I=I+1
1340 GOTO 1270
1350 GOSUB 6100
400 REM ***** IMPRIMME SUR ECRAN *****
1410 CLS:PRINT TAB(23)"RESULTATS":PRINT ""
1420 PRINT TAB(13)AB# TAB(33) Z#:PRINT ""
1430 FOR J= 2 TO (I-1)
1440 PRINT TAB(13) X(J) TAB(33) Y(J)
1450 NEXT

```

```

405 REM *      ROUTINE DE PREMIERE NUMERISATION      *
410 REM *****
415 CLS: SCREEN 2,0,0
420 LOCATE ,,0
425 REM *****  MENU DU TYPE DE GRAPHE *****
430 LOCATE 3,16:PRINT "NUMERISATION DE COURBE"
440 LOCATE 5,30:PRINT "TYPE D'AXES:"
445 LOCATE 7,40:PRINT "TYPE 1"
450 LOCATE 7,65:PRINT "TYPE 2"
455 LINE (300,70)-(470,100),,B
460 LINE (500,70)-(600,140),,B
465 LOCATE 10,37:PRINT "Y"
470 LOCATE 10,62:PRINT "Y"
475 LOCATE 14,49:PRINT "X"
480 LOCATE 19,70:PRINT "X"
490 LOCATE 14,5:PRINT "axes X  Y"
500 FOR J=1 TO 8
510 LOCATE (15+J),3:PRINT CH$(J)
520 NEXT J
525 LOCATE 25,4:PRINT "return POUR CONFIRMER"
530 REM ***** BOUCLE DE CHOIX *****
540 PT=00=0
550 ON KEY(1) GOSUB 680
555 ON KEY(2) GOSUB 685
560 ON KEY(3) GOSUB 690
565 ON KEY(4) GOSUB 695
570 ON KEY(5) GOSUB 700
575 ON KEY(6) GOSUB 705
580 ON KEY(7) GOSUB 710
585 ON KEY(8) GOSUB 715
590 ON KEY(9) GOSUB 670
595 ON KEY(10) GOSUB 670
600 KEY(1) ON :KEY(1) STOP
605 KEY(2) ON :KEY(2) STOP
610 KEY(3) ON :KEY(3) STOP
615 KEY(4) ON :KEY(4) STOP
620 KEY(5) ON :KEY(5) STOP
625 KEY(6) ON :KEY(6) STOP
630 KEY(7) ON :KEY(7) STOP
635 KEY(8) ON :KEY(8) STOP
640 KEY(9) ON :KEY(9) STOP
645 KEY(10) ON :KEY(10) STOP
650 RET#=INKEY$:IF RET#<>"" THEN IF ASC(RET#)=13 AND PT=1 THEN 720
660 GOTO 600
670 RETURN
680 PT=1:00=1:RETURN
685 PT=1:00=2:RETURN
690 PT=1:00=3:RETURN
695 PT=1:00=4:RETURN
700 PT=1:00=5:RETURN
705 PT=1:00=6:RETURN
710 PT=1:00=7:RETURN
715 PT=1:00=8:RETURN
720 REM ***** LECTURES DU NOM DES AXES *****
730 CLS
740 LOCATE 2,5:PRINT "ENTRE LE TITRE DU GRAPHE"
750 LOCATE 3,5,1
760 INPUT T1$
770 LOCATE 5,5:PRINT "TITRE EN ABSCISSE:"
780 LOCATE 6,5
790 INPUT AB$
800 LOCATE 8,5:PRINT "TITRE EN ORDONNEE:"
810 LOCATE 9,5
815 INPUT Z$
820 REM ***** LECTURES DES LIMITES DU GRAPHE *****
830 CLS:LOCATE 2,16 :PRINT "ENTREES DES LIMITES DU GRAPHE"

```



```

10 REM *****
20 REM *
30 REM *          PROGRAMME DE NUMERISATION
40 REM *
50 REM *          NUMERISATION DE GRAPHIQUE SUR PLOTTER HP 7475A
60 REM *
70 REM *          par DANIEL FAUCHON
80 REM *****
90 REM *****
1 REM *****
2 REM *
3 REM *          CONCU POUR DU PAPIER 8 1/2-11
4 REM *
5 REM *          PREVOIR UN SET-UP :  A4  US
6 REM *****
70 REM *****
85 REM *****
97 REM *          MENU PRINCIPAL
99 REM *****
100 KEY OFF
110 LOCATE 1,0
115 GOSUB 9000
120 CLS:LOCATE 5,16 :PRINT "CHOIX D'OPERATION"
140 FOR J=1 TO 6
150 LOCATE (7+J),10:PRINT CH$(B+J)
160 NEXT J
170 LOCATE 19,8:PRINT "return POUR CONFIRMER"
180 TP=TT=0
190 ON KEY(1) GOSUB 305
200 ON KEY(2) GOSUB 310
210 ON KEY(3) GOSUB 315
220 ON KEY(4) GOSUB 320
230 ON KEY(5) GOSUB 325
240 ON KEY(6) GOSUB 330
250 ON KEY(7) GOSUB 300
260 ON KEY(8) GOSUB 300
270 ON KEY(9) GOSUB 300
280 ON KEY(10) GOSUB 300
290 KEY(1) ON:KEY(1) STOP
300 KEY(2) ON:KEY(2) STOP
310 KEY(3) ON:KEY(3) STOP
320 KEY(4) ON:KEY(4) STOP
330 KEY(5) ON:KEY(5) STOP
340 KEY(6) ON:KEY(6) STOP
350 KEY(7) ON:KEY(7) STOP
360 KEY(8) ON:KEY(8) STOP
370 KEY(9) ON:KEY(9) STOP
380 KEY(10) ON:KEY(10) STOP
390 RET$=INKEY$:IF RET$<>" " THEN IF ASC(RET$)=13 AND TP=1 THEN 340
400 GOTO 240
410 RETURN
420 TP=1:TT=1:RETURN
430 TP=1:TT=2:RETURN
440 TP=1:TT=3:RETURN
450 TP=1:TT=4:RETURN
460 TP=1:TT=5:RETURN
470 TP=1:TT=6:RETURN
480 ON TT GOSUB 400,1200,2000,3000,4000,5000
490 GOTO 120
500 REM *****

```

APPENDIX 2

X-ray powder diffraction data (Reference [6])

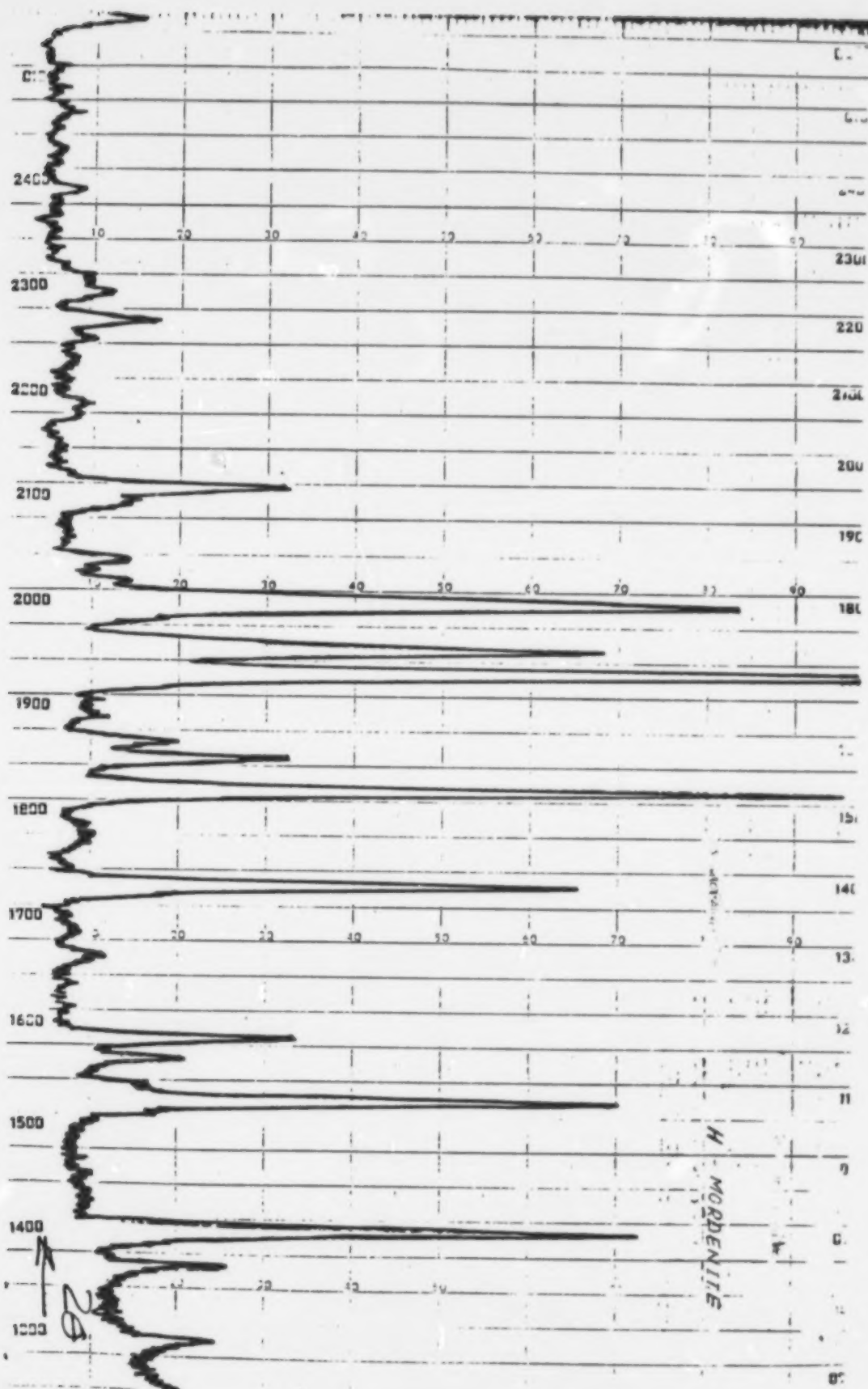
(Values in brackets: obtained data)

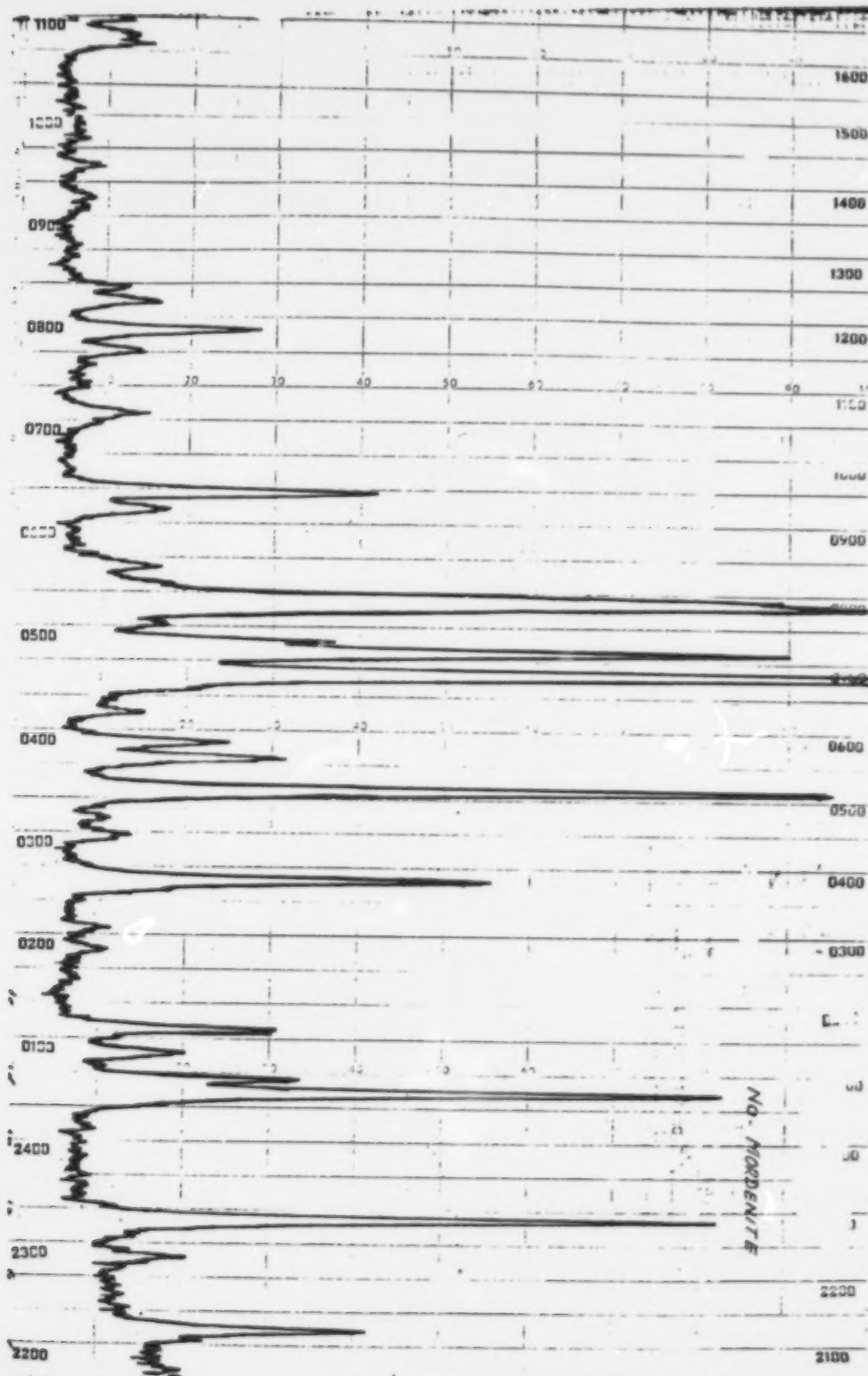
213

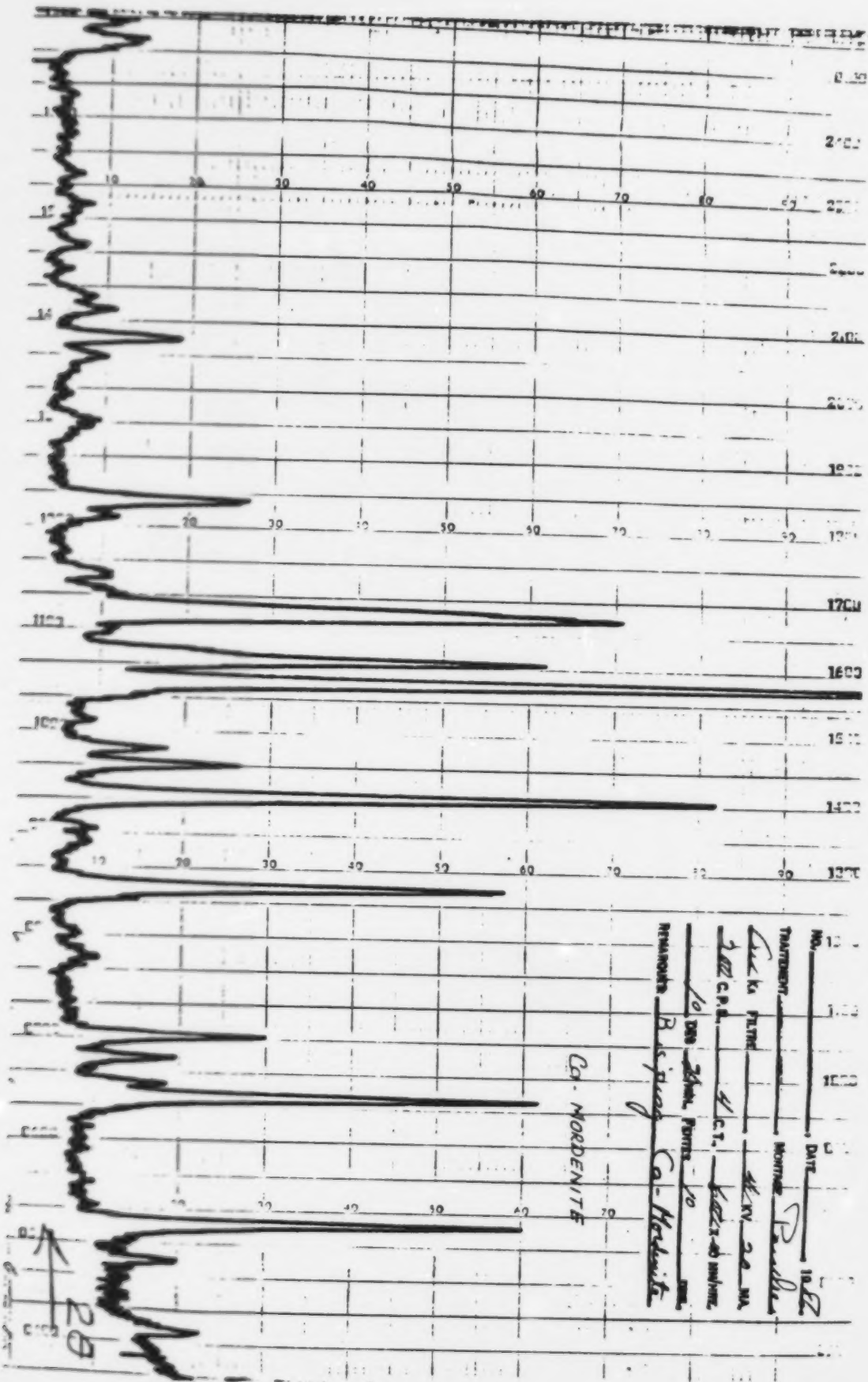
Na-mordenite	
d(Å)	I
(13.60)	
13.50	40
(10.40)	
10.20	10
(9.87)	
9.02	80
(6.56)	
6.51	50
(6.44)	
6.32	25
(6.11)	
6.01	10
(5.81)	
5.75	25
(5.06)	
5.03	2
(4.86)	
4.82	5
(4.55)	
4.50	40
(4.13)	
4.11	5
(3.99)	
3.96	70
(3.83)	
3.80	10
(3.75)	
3.72	10
(3.63)	
3.52	5
(3.49)	
3.44	100
(3.39)	
3.37	65
(3.32)	
3.28	10
(3.24)	
3.20	65
(3.11)	
3.13	10

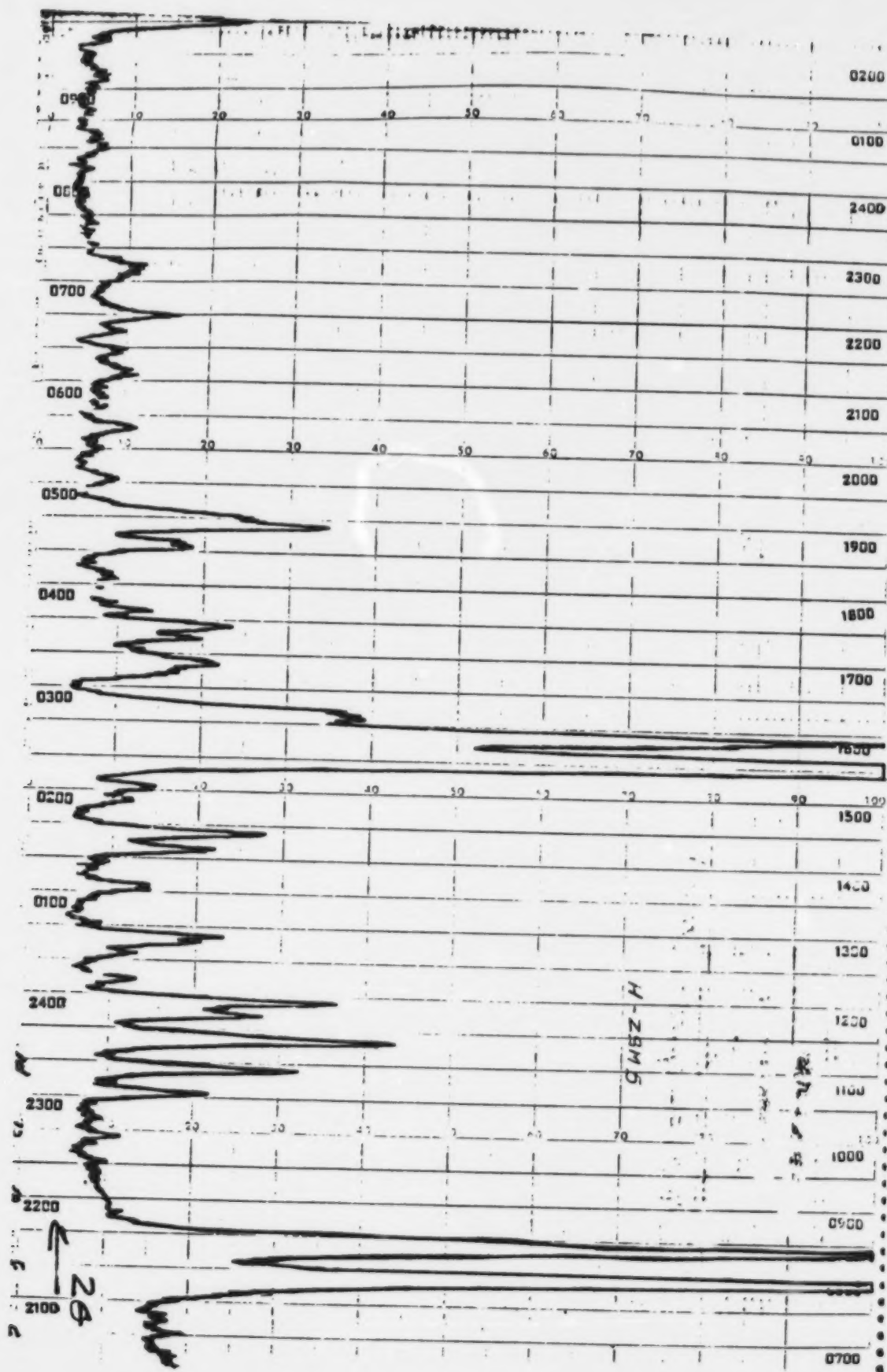
Na-x	
d(Å)	I
(14.73)	
14.47	100
(8.84)	
8.85	18
(7.69)	
7.54	12
(5.72)	
5.73	18
(4.80)	
4.81	5
(4.40)	
4.42	9
(4.23)	
4.23	1
(3.95)	
3.95	4
(3.79)	
3.81	21
-	
3.77	3
-	
3.61	1
-	
3.50	1
(3.36)	
3.34	8
3.25	1
(3.03)	
3.05	4
(2.93)	
2.94	9
(2.88)	
2.89	19
(2.80)	
2.79	8
(2.75)	
2.74	2

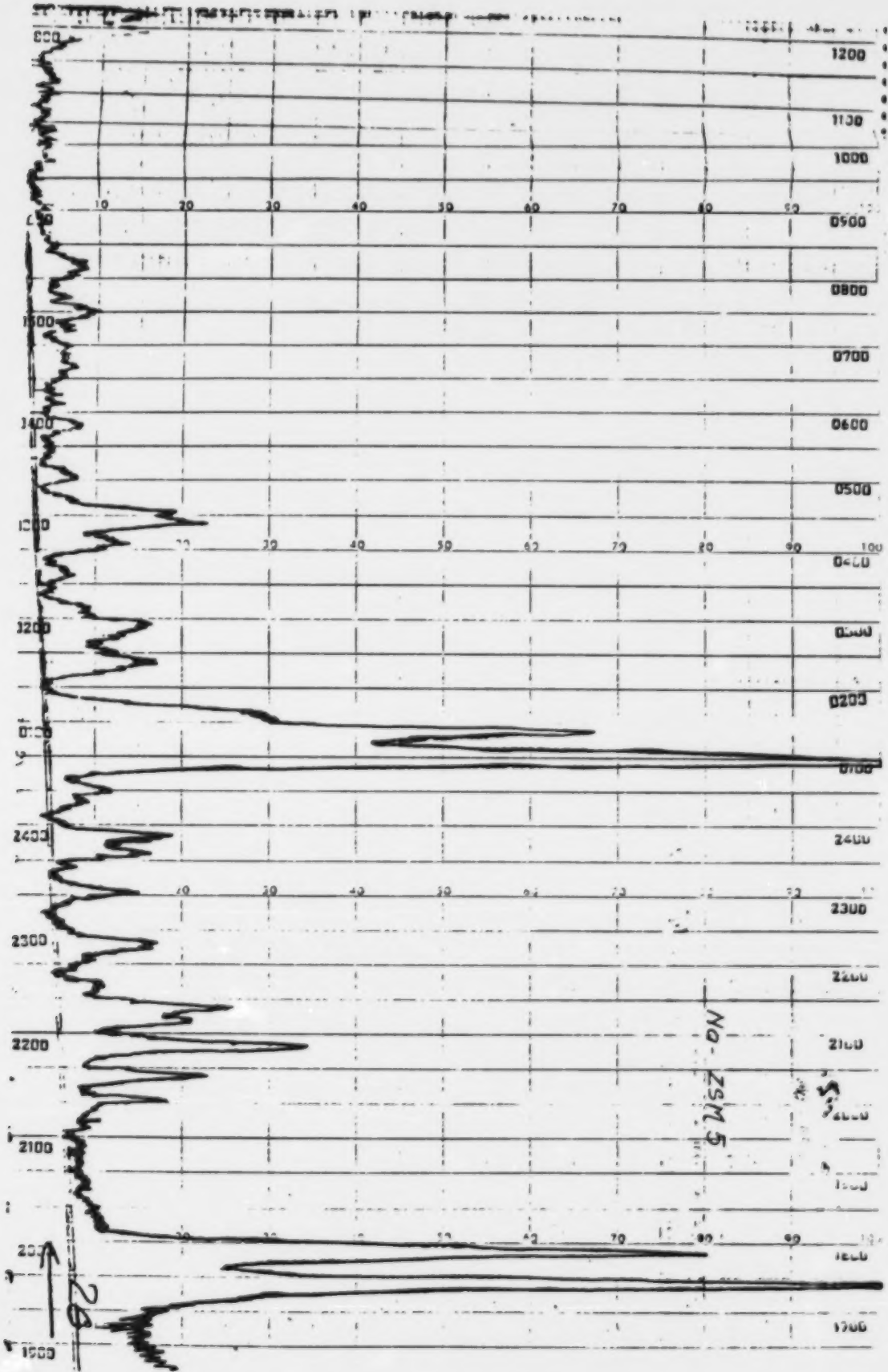
ZSM-5	
d(Å)	I
(11.40)	
11.36	29
(10.11)	
10.20	22
-	
9.07	8
(7.53)	
7.54	10
(7.08)	
7.17	7
(6.80)	
6.79	8
(6.37)	
6.45	11
(6.00)	
6.08	13
(5.72)	
5.77	10
(5.57)	
5.63	11
(5.37)	
5.42	5
(5.14)	
5.20	6
(5.00)	
5.05	8
(4.61)	
4.65	9
(4.40)	
4.40	12
(4.28)	
4.30	13
(4.09)	
4.12	7
(4.02)	
4.04	11
(3.86)	
3.86	100
(3.74)	
3.74	52
(3.63)	
3.62	51
(3.49)	
3.50	10
(3.45)	
3.46	13
(3.36)	
3.34	13
(3.31)	
3.28	8
(3.05)	
3.08	12
(3.00)	
3.01	16

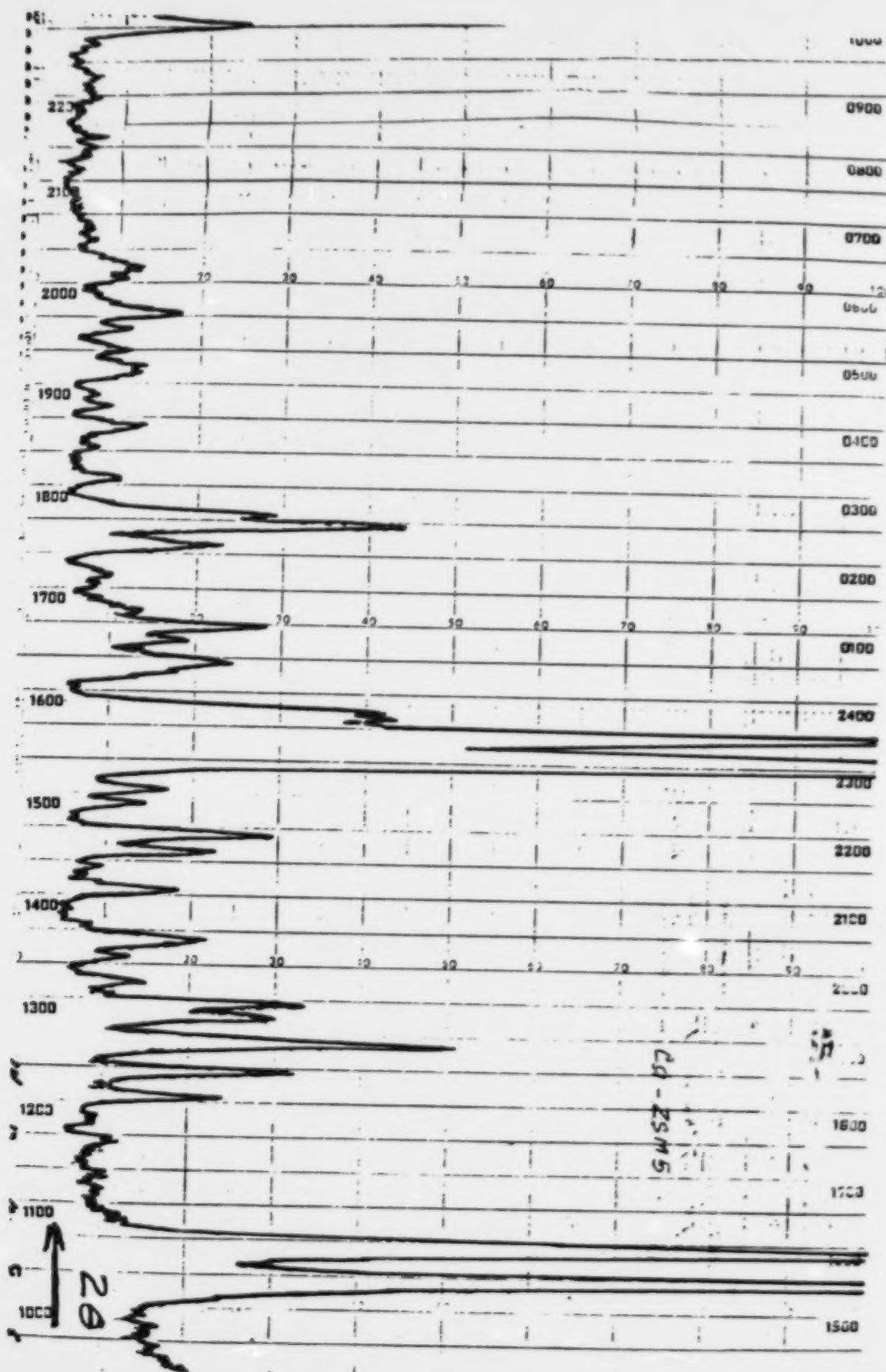


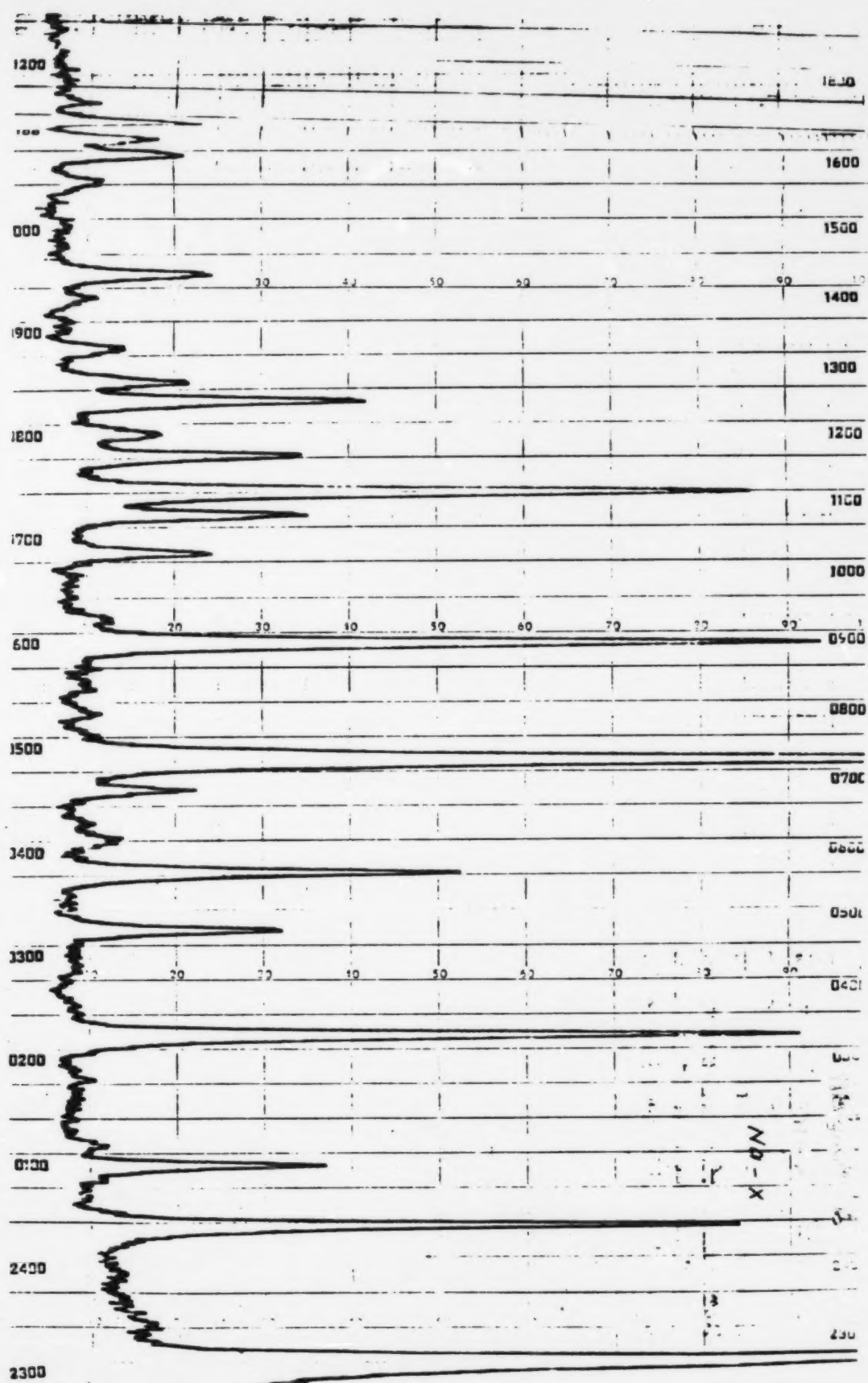












APPENDIX 3.1 - COMPUTER PROGRAM FOR THE CALCULATION OF MOMENTS FROM
EXPERIMENTAL DATA

3.2 - COMPUTER PROGRAM FOR THE ESTIMATION OF PARAMETERS BY
THE METHOD OF MOMENTS